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NOTE ON THE ACCELERATION OF SHIPS[1]

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Abstract

Calculations were made of the time and distance required for a ship to accelerate to any fraction of its maximum speed, and are intended to serve as a guide in determining the length of run to be made in approaching the measured course in the conduct of ship speed trials. The effect of inaccuracy in the underlying assumptions was examined. Curves and tables are presented and offered as suitable for use.

It has frequently been noticed that when a ship is making a speed trial on a course where the halfway point is marked, the mean speed over the second half of the course is higher than that over the first half (2, p. 416). Consideration of the ship acceleration problem shows that the acceleration continuously decreases as the speed approaches its maximum value, so that on either a space or time base the speed approaches its terminal value asymptotically. Of practical interest, during the conduct of speed trials of ships, is the question of how far the ship should be run in approaching the measured course to ensure that it will have reached a sufficient fraction of its true maximum speed. As a guide in this respect, calculations based on certain approximations for the characteristics of the ship have been made for the time and distance necessary to attain any speed.

Three assumptions have been made for the variation of thrust with speed. Two of these have been chosen to give upper and lower limits so that the effect of inaccuracy in the third, which has been adopted, may be studied. Using this approximation for thrust, the variation of the ship resistance has been dealt with; this yielded expressions for time and distance required to attain any speed in terms of quantities known for any ship.

Symbols

Let v = speed of ship in feet per second,

v_m = maximum speed of ship in feet per second,

r = water resistance of ship in pounds,

r_m = water resistance of ship at maximum speed,

f = effective thrust of propeller in pounds,

x = speed fraction = $\dfrac{v}{v_m}$,

t = time in seconds,

m = mass of ship + virtual mass of surrounding water in slugs,
s = distance in feet,
n = exponent of v in expression of ship resistance.

Thrust Variation Assumptions

The acceleration of a ship depends on the variation of effective thrust with speed. In reality this is determined by the manner in which the propellers are accelerated and by the characteristics of the propellers themselves. Some simplification is necessary if a mathematical treatment is required, and to this end three arbitrary assumptions have been made for the thrust-speed relation. Fig. 1 shows curves of thrust against speed, and Fig. 2 shows the consequent power-speed relation. The assumptions that determine these curves are outlined separately as follows.
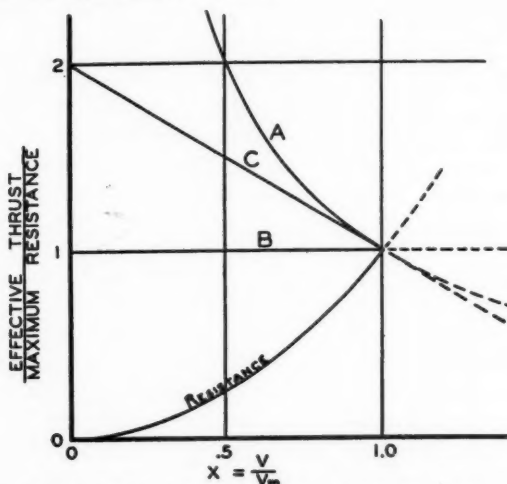

FIG. 1. *Curves showing the variations of propeller thrust with speed assumed for study.*
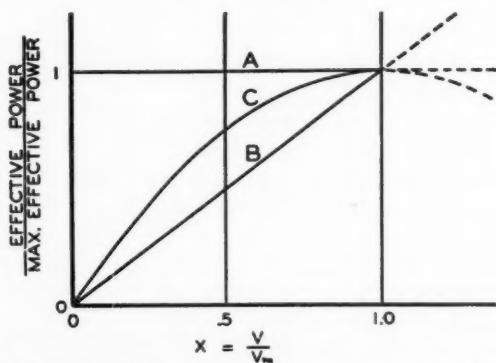
FIG. 2. *Curves showing the variation of effective power associated with the assumed thrusts.*

Case A   Upper Limit of Thrust

The upper limit of thrust is given by the condition that the effective power is constant throughout,

$$fv = \text{constant} = r_m v_m \ ,$$

hence
$$f = \frac{1}{x} \, r_m \ .$$

The thrust varies inversely with the speed, and as a consequence rises to an infinitely high value at zero speed, a condition obviously untrue. At the high speed end of the curve the assumption of constant effective power is probably quite close to real conditions.

Case B   Lower Limit of Thrust

A lower limit for thrust has been given by the assumption of a constant thrust, independent of speed,

$$f = r_m \ .$$

It is known that for a constant rotational speed the static thrust of a propeller is in general two or three times as great as the thrust at maximum efficiency, so that the above condition may be taken as a lower limit.

An inspection of the curve of effective power for this case shows that there is a departure from real conditions at the high speed end, where the curve should have a maximum value at $x = 1$ and hence a zero slope.

Case C   Linear Thrust Relation

The assumption is made that the thrust varies linearly with speed, beginning at a certain finite value and decreasing with speed.

$$f = a - bv \ .$$

The constants a and b are related to each other by satisfying the condition for maximum effective power when $v = v_m$, and are related to r_m by the fact that $f = r_m$ at the same point.

Effective power $= fv = av - bv^2$

$$\frac{d(EP)}{dv} = a - 2bv$$

$$= 0 \quad \text{when} \quad v = v_m \ ,$$

so that
$$a = 2bv_m$$
and
$$f = (2 - x) \, r_m \ .$$

The static thrust is, therefore, just twice the thrust at maximum speed. This is a reasonable value, and the shapes of the thrust and consequent power curves are also reasonable.

Resistance Variation Assumption

The water resistance of a ship may be fairly well approximated by an expression of the form,

$$r = kv^n \ ,$$

since
$$r_m = kv_m{}^n \ ,$$
$$r = x^n r_m \ .$$

If such an expression for resistance be chosen, it is important in the present instance to select n so that the portion of the resistance curve in the vicinity of $x=1$ is well approximated, since the greater portion of either space or time required for acceleration is taken up in this period when the speed is high and the acceleration is low.

The value of n must be selected from the known or calculated curve of ship resistance. For slow speed ships it is in the neighborhood of 2, but it increases to much higher values for medium and high speed ships.

The Mass to be Accelerated

Not only must the mass of the ship be accelerated but also the "virtual mass" of the surrounding water which is associated with its motion.

Theoretical work on the virtual mass of airships has shown that it is dependent upon the fineness ratio and particularly upon the shape and fineness of the ends (1, 3). The virtual mass of ship models was measured experimentally by von den Steinen (4), and the values obtained by him are sufficiently accurate for the present purpose. For the three models, a fishing boat, a freighter and a Maierform ship, the value for the virtual mass of the surrounding water was approximately 0.08 times the mass of the water displaced by the model.

For practical purposes of acceleration calculations, m may be taken as 1.08 times the mass of the ship.

The Equation of Motion and its Solution

The equation of motion for the ship is

$$m\frac{dv}{dt} = f - r \ . \tag{1}$$

Changing the variable from v to x gives

$$mv_m\frac{dx}{dt} = f - r \ ,$$

f and r, however, are functions of x, according to the different thrust and resistance assumptions made above. Separation of the variables and integration gives the following expressions for the time,

$$\text{Case } A \qquad t = \left(\frac{mv_m}{r_m}\right)\int \frac{x\,dx}{1-x^{n+1}} \ + \text{constant} \ ,$$

$$\text{Case } B \qquad t = \left(\frac{mv_m}{r_m}\right)\int \frac{dx}{1-x^n} \ + \text{constant} \ ,$$

$$\text{Case } C \qquad t = \left(\frac{mv_m}{r_m}\right)\int \frac{dx}{2-x-x^n} + \text{constant} \ .$$

Substitution for dt in the equation of motion,

$$xv_m = v = \frac{ds}{dt}$$

$$dt = \frac{ds}{xv_m}$$

gives

$$mv_m^2 x\frac{dx}{ds} = f - r \ .$$

By separation of the variables, and integration, the following equations for the distance are obtained.

$$\text{Case } A \qquad s = \left(\frac{mv_m{}^2}{r_m}\right)\int \frac{x^2 dx}{1-x^{n+1}} \quad + \text{constant},$$

$$\text{Case } B \qquad s = \left(\frac{mv_m{}^2}{r_m}\right)\int \frac{x dx}{1-x^n} \quad + \text{constant},$$

$$\text{Case } C \qquad s = \left(\frac{mv_m{}^2}{r_m}\right)\int \frac{x dx}{2-x-x^n} + \text{constant}.$$

It is seen that the general form of the expression for t is

$$t = \left(\frac{mv_m}{r_m}\right) F_T(x),$$

and for s it is

$$s = \left(\frac{mv_m{}^2}{r_m}\right) F_S(x),$$

where $F_T(x)$ and $F_S(x)$, which may be called the time factor and space factor, respectively, are functions of the non-dimensional speed fraction x and the exponent n. It will be noticed that the bracketed quantities, $\left(\frac{mv_m}{r_m}\right)$ and $\left(\frac{mv_m{}^2}{r_m}\right)$, have the dimensions of time and length, respectively, and that the use of any congruent system of units besides the foot-pound-second system suggested, is permissible.

For the comparison of the three assumptions regarding the thrust, the space and time factors can be evaluated. The integrals have been solved for certain integral values of n, and the constants of integration were determined by putting t and s each equal to zero when $x=0$. The case of $n=2$, which applies to all slow ships (where the resistance is predominantly skin friction), yields the following:

Case A $\quad F_T(x) = \frac{1}{3}\left[\frac{1}{2}\log\frac{(1+x+x^2)}{(1-x)^2} + \sqrt{3}\arctan\frac{2x+1}{-\sqrt{3}} - \sqrt{3}\arctan\frac{-1}{\sqrt{3}}\right]$

$\qquad\qquad F_S(x) = -\frac{1}{3}\log(1-x^3),$

Case B $\quad F_T(x) = \frac{1}{2}\log\frac{(1+x)}{(1-x)}$

$\qquad\qquad F_S(x) = -\frac{1}{2}\log(1-x^2),$

Case C $\quad F_T(x) = \frac{1}{3}\left[\log\frac{(2+x)}{(1-x)} - \log 2\right]$

$\qquad\qquad F_S(x) = -\frac{1}{3}\left[\log\{(2+x)^2(1-x)\} - \log 4\right].$

Tables I and II of $F_T(x)$ and $F_S(x)$, respectively, for the three cases for values of x between 0.9 and 0.999, have been computed. The computed values have been plotted and are shown in Figs. 3 and 4 for direct comparison (for convenience the arbitrary base of $-\log(1-x)$ was used).

TABLE I

TIME FACTORS $F_T(x)$

x	Case A	Case B	Case C					
	$n=2$	$n=2$	$n=2$	$n=2.5$	$n=3$	$n=3.5$	$n=4$	$n=10$
0.900	0.52	1.47	0.89	0.83	0.78	0.75	0.72	0.62
0.950	0.76	1.83	1.13	1.03	0.96	0.91	0.87	0.70
0.980	1.06	2.30	1.44	1.30	1.20	1.12	1.06	0.79
0.990	1.29	2.64	1.67	1.50	1.39	1.28	1.21	0.86
0.995	1.52	2.99	1.90	1.70	1.55	1.43	1.35	0.93
0.997	1.69	3.25	2.07	1.84	1.68	1.55	1.42	0.97
0.999	2.06	3.80	2.44	2.16	1.95	1.79	1.67	1.07

TABLE II

SPACE FACTORS $F_S(x)$

x	Case A	Case B	Case C					
	$n=2$	$n=2$	$n=2$	$n=2.5$	$n=3$	$n=3.5$	$n=4$	$n=10$
0.900	0.44	0.83	0.52	0.47	0.44	0.41	0.40	0.32
0.950	0.65	1.16	0.74	0.66	0.61	0.56	0.54	0.39
0.980	0.94	1.61	1.04	0.92	0.84	0.77	0.72	0.48
0.990	1.17	1.96	1.27	1.12	1.01	0.92	0.86	0.55
0.995	1.40	2.30	1.50	1.31	1.18	1.07	1.00	0.62
0.997	1.57	2.56	1.67	1.46	1.31	1.19	1.08	0.66
0.999	1.94	3.11	2.03	1.77	1.58	1.43	1.32	0.76
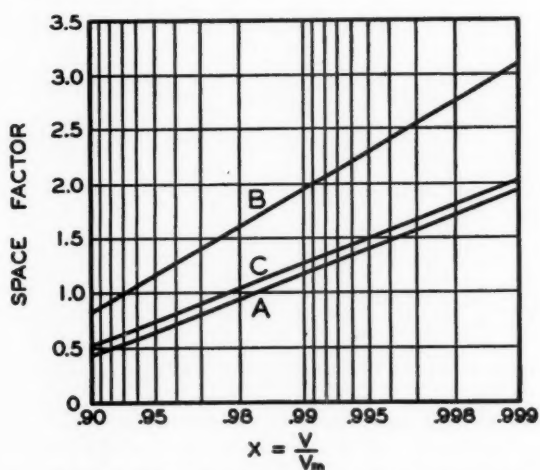
FIG. 3.   Curves of space factor against speed fraction for each of the three thrust assumptions.
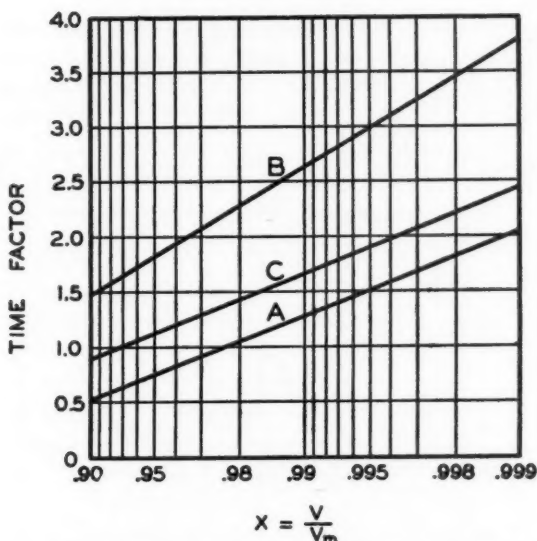
FIG. 4.   *Curves of time factor against speed fraction for each of the three thrust assumptions.*

Comparison of Thrust Assumptions

A study of Figs. 3 and 4 will show that the space and time factors are of the same order of magnitude for each of the three cases. The effect of the thrust assumption is greater upon the time factor than upon the space factor. Cases A and C give nearly equal space factors, and any thrust curve (Fig. 1) lying between them will produce space factors between those shown (Fig. 3). It is believed that real thrust curves would generally fall between the A and C, but closer to the C case, so that the space factors given by the thrust assumption C are probably sufficiently accurate for general use. The variation of the time factor is determined chiefly by the thrust at very low speeds, and it is at low speeds that the three assumptions differ most. However, the time factor is not so useful as the space factor, and, moreover, if the integration of the time equations is begun at values of x far above zero, the variation diminishes greatly.

Variation of n

If the Case C thrust assumption is adopted, the effect of variation of the exponent n in the expression for resistance upon the time and space factors can be studied.

For the general case

$$F_T(x) = \int_o^x \frac{dx}{2-x-x^n}$$

and

$$F_S(x) = \int_o^x \frac{xdx}{2-x-x^n} \ .$$

For the specific case $x=2$, the integrals have been given, and for the case $n=3$ they are

$$F_T(x) = \tfrac{1}{8}\left[\log \frac{(2+x+x^2)}{(1-x)^2} + \frac{6}{\sqrt{7}} \arctan \frac{2x+1}{\sqrt{7}} - \log 2 - \frac{6}{\sqrt{7}} \arctan \frac{1}{\sqrt{7}}\right]$$

and $F_S(x) = \tfrac{1}{8}\left[\log \frac{(2+x+x^2)}{(1-x)^2} - \frac{10}{\sqrt{7}} \arctan \frac{2x+1}{\sqrt{7}} - \log 2 + \frac{10}{\sqrt{7}} \arctan \frac{1}{\sqrt{7}}\right]$

FIG. 5.   *Curves of time factor against resistance exponent for various speed fractions, using linear thrust assumption.*

$$n = \frac{\log \frac{V}{V_m}}{\log x}$$

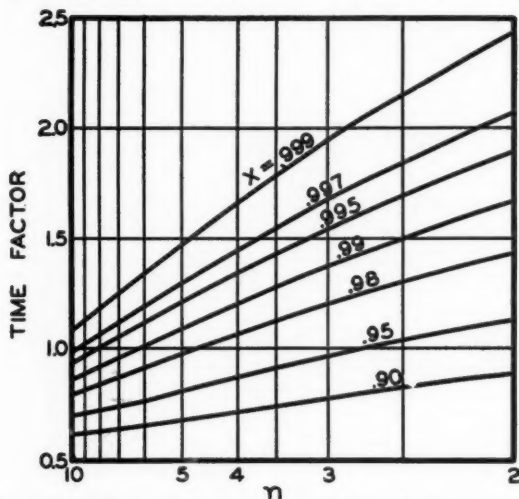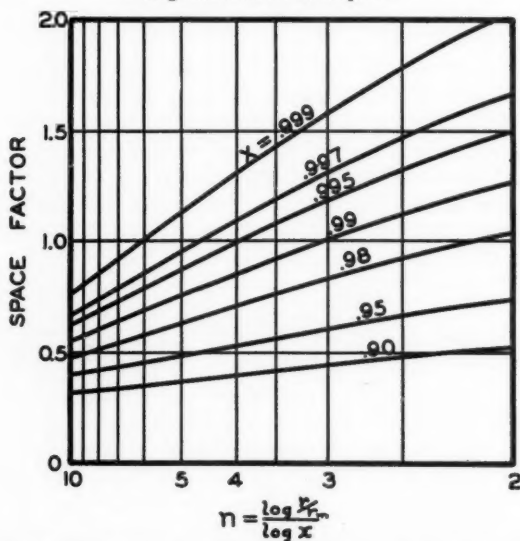FIG. 6.   *Curves of space factor against resistance exponent for various speed fractions, using linear thrust assumption. These curves are suggested for use.*

The numerical values of the space and time factors for non-integral values of n, and for integral values greater than 3, can be obtained by approximate methods for any particular value of x. This has been done for $n = 2.5, 3.5, 4$ and 10, and the results are shown in Tables I and II.

Curves of the space and time factors plotted against n (on an arbitrary base of $1/n$ which allowed plotting the values for $n = \infty$) are shown in Figs. 5 and 6.

The interpolation for any value of n between 2 and 10 may easily be made.

Application and Numerical Example

In applying the time and space factors to a specific case the following steps must be taken.

(i) From the design data of the ship obtain

    (a) The resistance r_m at maximum speed in pounds.

    (b) The exponent n for the variation of resistance.

    (c) The total mass to be accelerated $= 1.08 \times$ mass of ship
       ($m = 75 \times$ displacement of ship in long tons).

    (d) The anticipated maximum speed, v_m, in feet per second
       ($v_m = 1.689 \times$ max. speed in knots).

(ii) Compute the time and space products, $\left(\dfrac{mv_m}{r_m}\right)$ and $\left(\dfrac{mv_m^2}{r_m}\right)$.

(iii) From Figs. 5 and 6 select the values of space and time factors for the desired speed fraction.

(iv) Compute times and distances by multiplying products and factors found in (ii) and (iii).

Example

It is desired to know how far a certain ship must be run to attain 99.5% of its maximum speed.

The values assumed are:

        $r_m = 1,250,000$ lb.

        $\Delta = 80,000$ long tons,

hence $m = 75 \times 80,000 = 6,000,000$ slugs,

        $n = 3$

        $v_m = 32$ knots $= 32 \times 1.689 = 54$ ft. per sec.

The time product, $\dfrac{mv_m}{r_m} = \dfrac{6 \times 10^6 \times 54}{1.25 \times 10^6} = 259$ sec.

The space product, $\dfrac{mv_m}{r_m} = 259 \times 54 = 14,000$ ft.

From the tables, F_T (0.995) and F_S (0.995) are 1.55 and 1.18, respectively.

The time required is, therefore, $1.55 \times 259 = 402$ sec., and the space covered is $1.18 \times 14,000 = 16,500$ ft.

The above calculations are based on starting from rest.

Conclusion

It is believed that the distances computed by the above outlined methods will be useful as a guide to persons conducting speed trials of ships in ensuring that the desired speed has been obtained, without making an unnecessarily long approach run.

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NOTE ON THE EUPATHEOSCOPE AND THE MEASUREMENT OF EQUIVALENT TEMPERATURE IN CANADA[1]

By C. D. Niven[2]

Abstract

Readings have been taken on the eupatheoscope and compared with readings on thermometers and with readings on the A.S.H.V.E. effective temperature chart. It was found that the mean of the readings on two thermometers, situated one at the floor level and one at the level of the head of a sedentary worker, gave a value fairly close to the reading on the eupatheoscope. The general conclusion is reached that elaborate apparatus for reading comfort temperature is not justified until an explanation has been given of what constitutes the "freshness" of air, but that in Canada in rating comfort conditions more attention should be paid to temperature gradients, which are pronounced during spells of zero weather.

Introduction

There is perhaps no country in the world, with the exception of Siberia, to which a knowledge of indoor atmospheric conditions is of greater importance than it is to Canada. In most parts of the northern portion of the American continent windows cannot be kept wide open for at least six months of the year, and in some parts it is uncomfortable if fresh air is allowed to enter by the window during several months of the year. Such conditions put a strain on the respiratory organs which of course function most perfectly when fresh outdoor air is breathed. In spite of the obvious importance of the heating and ventilating problem in Canada, little work is being done on it. As an introduction to this work a eupatheoscope was imported from England to ascertain whether the indications it gave corresponded with the sensation of comfortable warmth felt indoors in Canada. The problem of ventilation greatly depends upon the maintenance of the conditions that give a comfortable sensation of warmth, for no matter how health-giving a ventilation scheme is, the public will undoubtedly reject it if it makes the room uncomfortably cold.

Observations taken on the eupatheoscope are given in this communication. These are compared with readings taken on thermometers.

The eupatheoscope is an instrument designed by Dufton (2). It gives a measure of the cooling power of the air in a room. It takes account of the temperature of the air, the air movement and the radiant heat energy in the room, but it does not take account of the humidity of the air. The eupatheoscope consists of a blackened cylinder about 22 in. high and $7\frac{1}{2}$ in. in diameter. The temperature of this cylinder is kept constant by means of a thermostat controlling the amount of heat supplied internally, and this amount of heat is estimated by the distance the mercury is forced down an inverted thermometer. Obviously, the more the mercury expands, the cooler the room must

be because cold atmospheric conditions imply that heat must be supplied to the cylinder in order that its temperature be kept constant.   This ingenious device appeals to one because the principle on which it operates resembles the principle employed by the human body.   In the human body the thermostatic control is said to be on the face, and when the face is exposed to cold the human system automatically generates more heat.

Man's feeling of comfort depends primarily on his physiological state at the moment.   Therefore, any comparison between results obtained by means of a mechanical instrument and the feeling of comfort of a human being cannot be consistent.

Results

At the beginning of the investigation the readings on the eupatheoscope were compared with the effective temperatures as determined for a particular temperature and humidity from the "still air" chart in the A.S.H.V.E. guide book.   It was found that the two figures differed by several degrees, and since the eupatheoscope did not take account of the relative humidity the difference was not constant.   The readings are shown in the first thirteen lines of Table I. A series of readings were taken to compare the eupatheoscope readings with readings on certain thermometers placed in the following positions:—(1) outside the window close to the glass; (2) inside the window close to the glass; (3) close to the floor, near the eupatheoscope; (4) $4\frac{1}{4}$ ft. from the floor, close to the eupatheoscope. The thermometers in Positions (3) and (4) were hung from a vertical stick so that the temperature at the head and the feet of one who might be sitting at a desk would be known.   It might be mentioned that the eupatheoscope and the thermometers at Positions (3) and (4) were situated about eight feet from the window and that a desk was standing between them and the window.   The radiator, which was not always in use, was situated under the window.

The mean of the temperatures (Table I) read on the thermometers at the top and at the bottom of the vertical stick near the eupatheoscope differed by only a small amount from the eupatheoscope reading.   On January 9, readings on the psychrometer were again begun.   In the lower part of Table I a record is given of the temperatures read on the thermometers, the eupatheoscope reading, and the effective temperature as determined from the A.S.H.V.E. chart.   These data substantiated the conclusions reached previously, namely, that the eupatheoscope reading did not agree with the effective temperature shown by the A.S.H.V.E. chart, but that it differed very little from the mean of the two temperatures read on the thermometers hung on the vertical stick.

The difference between the eupatheoscope reading and the reading taken from the "effective temperature" chart is given in Table I.   It is interesting to note that the large differences between these two figures arise generally when the room temperature is high. Thus it can be understood that in England the eupatheoscope is a better indicator than it is in Canada because the houses

TABLE I

Date	Wind	Temp. outside window, °F.	Temp. inside window, °F.	Temp. on floor, °F.	Temp. at head, °F.	Mean temp. at floor and head, °F.	Room temp. on desk, °F.	Room humidity	Effective temp., F°	Eupatheoscope reading	Eupatheoscope—Eff. temp., °F.	Mean temp., °F., at floor and head—eupatheoscope	Head-floor temps., °F.	Remarks
Sept. 12							73.5	61	70	75	5			
15							74	65	70.5	76.5	6			
17							72.5	53	68	73.5	5.5			
18							69	47	65	68.5	3.5			
19							70	55	66.5	69	3.5			
20							69	59	65.5	67.5	2.0			
Oct. 2							67	45	63.5	65	1.5			
3							67	53	63.5	66	2.5			
4							67	49	63.5	64	0.5			
5							67	45	63.5	65	1.5			
7							65	44	61.5	65	3.5			
16							67	41	63	66	3.0			
Nov. 14							62	34	59	61	2.0			
Dec. 5		27	55	61	62	61.5				61.5		0	1.0	
6	NW	18	52	60	62	61				60.5		0.5	2.0	
6		17	55	61	63	62				62		0	2.0	
7	NW	8	50	57	60	58.5				59		0.5	3.0	
8	NE	6	52	57	60	58.5				58.5		0	3.0	
10	NW	13	72	63.5	68	66				65.5		0.5	4.5	Rad. on
10		20	55	61	63.5	62.5				62.5		0	2.5	Rad. off
11	N	8	53	58	62	60				59.5		0.5	4.0	Rad. off
11		20	80	64.5	67.5	66				65.5		0.5	3.0	Rad. on
11		18	56	62	64	63				63.5		0.5	2.0	Rad. off
12	N	16	55	60	62	61				61		0	2.0	
13		28	56	60.5	63	62				62		0	2.5	
14	N	22	54	59	61.5	60.5				60.5		0	2.5	
15	WNW	8	42	56	60	58				58.5		0.5	4.0	
17		21	80	71	73	72				72.5		0.5	2.0	Rad. on
18	W	6	48	61	64	62.5				63		0.5	3.0	
19	E	22	88	72	75.5	74				74		0	3.5	Rad. on
20		20	65	70	71	70.5				69.5		1.0	1.0	Rad. on
21	E	16	64	71	73	72				72.5		0.5	2.0	Rad. on
22	N	12	82	71.5	74	73				73		0	2.5	Rad. on
25	No wind	19	86	73	75	74				74		0	2.0	Rad. on
26		− 6	49	55	59	57				57		0	4.0	
27	E	12	88	70	74	72				73		1.0	4.0	Rad. on
28	E	17	58	63	66	64.5				63.5		1.0	3.0	
31		− 3	46	53	57	55				55		0	4.0	
Jan. 2	NW	− 5	60	63	70	67.5				67		0.5	7.0	Rad. on
3	NE	12	60	70	72.5	71.5				71.5		0.0	2.5	Rad. on
4	NW	−12	57	69	75	72				73		1.0	6.0	Rad. on
5	NE	1	66	73	78	75.5				77		1.5	5.0	Rad. on
7		43	68	74	76	75				75.5		0.5	2.0	Rad. on
7		46	66	62	66	64				66		2.0	4.0	Window open.
8		43	85	72	74	73				73.5		0.5	2.0	Rad. on
9	N	33	62	67	68.5	68	69	32	64.5	67.5	3.0	0.5	1.5	
10		40	65	68.5	69.5	69	70	33	65	68.5	3.5	0.5	1.0	
11	NW	21	54	62	65.5	64	66	21	61	64.5	3.5	0.5	3.5	
12	N	2	51	59	62	60.5				60		0.5	3	
12		3	59	62	65.5	64	64	15	60	64	4.0	0	3.5	Rad. on
14	N	12	73	71.5	75	73.5	73.5	13	66	73.5	7.5	0	3.5	Rad. on
15	NE	− 1	78	72	77	74.5	76	16	68.5	76	7.5	1.5	5	Rad. on
16	N	3	57	64	68	66	67	21	62	66	4	0	4	
17	SE	10	57	63	66	64.5	64.5	23	60.5	64	4	0	3	
19		0	58	66	68.5	67	68	20	63	67	4	0	2.5	
21	E	28	64	69	70	69.5	70	25	64.5	69	4.5	0.5	1.0	
22	N	4	53	64	66	65	65	27	60	64	4	1.0	2.0	
23	NE	2	56	63	68	65.5	67	20	62	66	4	0.5	5.0	Door open
24	NE	−14	45	69	73	71	71	17	64.5	70.5	6	0.5	4.0	Rad. on
25	W	− 5	92	71	76	73.5	75	12	67	74	7	0.5	5.0	Rad. on
26	N	− 1	60	72	76	74	74	20	67	74	7	0	4 0	

in England are usually kept at temperatures ranging from 60° to 66° F., not at 72° F. Another point of interest is the fact that the temperature gradient given in the second last column of the table is greatest during the periods when the outdoor temperature is lowest. Some observations made during the summer, which are not reported here, serve to accentuate this. During the summer the temperature gradient was usually zero or one degree.

During the following winter more observations were taken, and these are given in Table II. As the wind directions and the readings on the thermometer placed inside the window were not useful, they were not noted. The correspondence between the eupatheoscope reading and the mean of the two thermometers on the stick is not so good in this table. It would appear, however, that this is not entirely a contradiction of our inference from Table I, since the table shows that it is just when the agreement between those figures was poor that the eupatheoscope reading differed less than usual from the effective temperature reading. Since the eupatheoscope did not appear to hold its calibration accurately, one is inclined to think that the readings on it were at times too high. In this connection it is interesting to note that if 4 be subtracted from the mean of the readings on the thermometers, the resulting figure does not differ very much from the effective temperature readings recorded in Table II.

One is inclined, therefore, to believe that two thermometers, one hung vertically above the other with their bulbs $\frac{1}{4}$ in. and $4\frac{1}{4}$ ft. from the floor, give an indication of the equivalent temperature in a room in which there is comparatively little air movement, no strong sources of heat radiation and not too extreme temperatures and humidities. Thus the thermometers supply in a simple manner the information that the eupatheoscope or the A.S.H.V.E. chart would supply under the said restricted conditions. The fact that the eupatheoscope did not hold its calibration well, detracts from its suitability, while the use of the A.S.H.V.E. chart necessitates the use of a psychrometer. Thermometers placed vertically one above the other in this way give an estimate of the temperature gradient, which is information of substantial importance in the evaluation of comfort conditions for the sedentary worker.

Sir Leonard Hill pointed out that a higher cooling power on the feet than on the head gives rise to discomfort, yet no account of this is usually taken in discussing comfort temperatures. In addition to room temperature, relative humidity and air movement, it is desirable in determining conditions for comfort in the winter time to take into account the temperature gradient, or, to be more accurate, the "cooling power gradient". The discovery of the large temperature gradients in the room to which the above data refer explains why the room felt uncomfortably cold even when the thermometer reading was high enough.

In an article (1, p. 55) by Angus the uncomfortable effect of high cooling power on the feet is stressed. Referring to an investigation on board ship he writes:—"But the dynamo-room was considered to be the most uncomfortable

TABLE II

Date		Temp. outside window, °F.	Temp. on floor, °F.	Temp. at head, °F.	Mean temp. at floor and head, °F.	Room temp. on desk, °F.	Room humidity	Effective temp., °F.	Eupatheoscope reading	Eupatheoscope —Eff. temp., °F.	Mean temp. (°F), floor and head—eupatheoscope	Head-floor temps, °F.
Aug.	31	61.0	70.0	71.0	70.5	71.0	48.0	66.5	68.0	1.5	2.5	1.0
Sept.	5	67	70	71	70.5	71	52	67	67.5	0.5	3.0	1.0
	6	60	70	70	70	70	55	66.5	67.5	1.0	2.5	0
	7	59.5	70	70	70	70	51	66	67	1.0	3.0	0
	19	68	73	73	73	73	65	70	73	3.0	0	0
	20	60	72	73	72.5	73	63	69.5	73.5	4.0	1.0	1.0
	21	58	72	73	72.5	72.5	53	68.5	72.5	4.0	0	1.0
	23	46	67	69	68	69	47	65	67.5	2.5	0.5	2.0
	24	52	68	70	69	70	51	66	68.5	2.5	0.5	2.0
	25	57	69	70	69.5	70	51	66	69	3.0	0.5	1.0
Oct.	31	51	72	72	72	72	49	67.5	70.5	3.0	1.5	0
Nov.	1	51	71	72	71.5	71	45	66.5	70.5	4.0	1.0	1.0
	2	43	70	71	70.5	70	51	66	69.5	3.5	1.0	1.0
	4	48	68	68.5	68	68	38	64	67	3.0	1.0	0.5
	5	62	70	70	70	70	55	66.5	69	2.5	1.0	0
	6	41	68	69	68.5	69	39	64.5	68	3.5	0.5	1.0
	7	39	70	71	70.5	71	33	65.5	70	4.5	0.5	1.0
	8	45	70	72	71	71	33	65.5	71	5.5	0	2.0
	9	37	70	72	71	71	30	65.5	70	4.3	1.0	2.0
	12	36	72	73	72.5	72.5	34	67	72	5.0	0.5	1.0
	13	38	68	70	69	69	35	64.5	68	3.5	1.0	2.0
	14	41	68	69	68.5	69	35	64.5	67	2.5	1.5	1.0
	15	39	66	67	66.5	67	37	62.5	65	2.5	1.5	1.0
	16	32	64	65.5	65	65	35	61.5	63	1.5	2.0	1.5
	18	32	64	65	64.5	65	27	61	62.5	1.5	2.0	1.0
	19	34	66	67	66.5	66	29	61.5	64	2.5	2.5	1.0
	20	45	68.5	69.5	69	68.5	47	65	67.5	2.5	1.5	1.0
Dec.	17	19	61	63	62	62	20	58	60.5	2.5	1.5	2.0
	18	26	63	66	64.5	55	44	61.5	62.5	1.0	2.0	3.0
	19	28	67	69	68	67	33	62.5	66	3.5	2.0	2.0
	20	18	66	68	67	67	30	62.5	66	3.5	1.0	2.0
	21	0	58	63	60.5	60.5	15	57	60	3.0	0.0	5.0
	23	0	59	63	61	60.5	20	57	60	3.0	1.0	4.0
	26	6	59	62	60.5	60	21	57	58.5	1.5	2.0	3.0
	27	12	57	60	58.5	58	23	55.5	57	1.5	1.5	3.0
	28	−3	55	59	57	57	17	55	55.5	0.5	1.5	4.0
	30	0	58	62	60	60	17	57	57.5	0.5	2.5	4.0
	31	8	62	65	63.5	63	21	59	61	2.0	2.5	3.0
Jan.	2	32	64	66	65	65	24	61	63	2.0	2.0	2.0
	3	36	66	68	66	67	26	62	64.5	2.5	1.5	2.0
	4	36	66	67	66.5	66.5	27	62	64.5	2.5	2.0	1.0
	7	32	68	70	69	68	23	63	67	4	2.0	2.0
	8	13	64	67	65.5	65	24	60.5	64	3.5	1.5	3.0
	9	22	65	67	66	64	26	60	64	4	2.0	2.0
	10	34	66	68	67	67	26	62	64.5	2.5	2.5	2.0
	11	34	65	68	66.5	66.5	26	62	64.5	2.5	2.0	3.0
	13	32	67	69	68	68	31	63.5	67	3.5	1.0	2.0
	14	2	59	63	61	61	27	57.5	60	2.5	1.0	4.0
	15	16	62	65	63.5	63	25	59.5	61.5	2.0	2.0	3.0
	16	8	58	62	60	60	21	57	57.5	0.5	2.5	4.0
	17	4	61	63	62	63	17	59	60	1.0	2.0	2.0
	18	8	71	75	73	74	17	66.5	71	4.5	2.0	4.0
	20	6	58	62	60	60	21	57	57	0	3.0	4.0
	21	4	72	76	74	75	18	67	72.5	5.5	1.5	4.0
	22	30	64	67	65.5	66	29	60.5	63.5	3.0	2.0	3.0
	23	−6	54	59	56.5	57	14	54.5	57	2.5	0.5	5.0
	24	−8	65	70	67.5	69	43	65	64.5	0.5	3.0	5.0

part of the engineers" 'tween decks'. Here I found that although on the days in question the temperature was only two degrees above that in the engine-room with the fans on, a very high air velocity along the deck was causing a reversal of cooling powers—hot heads and cold feet."

The fact that the human thermostat is situated on the face makes a high temperature gradient disagreeable for anyone whose feet cool easily. The writer asked a number of persons whether they complained first of cold on the feet or cold on the body, and there was found to be a considerable difference of opinion, while many could not answer at all. Nevertheless the evidence of both Hill and Angus is sufficient to warrant the consideration that temperature gradient is an item that must be taken into account by a physical instrument designed especially to measure comfort conditions, particularly in localities exposed to subzero weather.

Conclusions

To sum up, it may be said that the work indicated that the eupatheoscope did not give results agreeing with A.S.H.V.E. chart: the disagreement was largest when the temperature was high and the humidity low: on such days the temperature gradient was often large. In England, where the eupatheoscope was developed, these gradients would not be nearly so important as in Canada, since it is during subzero weather that they are as a rule largest. The instrument that would be required in Canada would need to be one in which temperature gradient was taken into account, as well as the mere cooling power of the air.

Such an instrument would undoubtedly be rather elaborate; strictly speaking it should measure the cooling power of the air at the feet as well as at the head. But even if it were constructed it might still not give an estimate of comfortable indoor atmospheric conditions as it would not detect the effect of air-conditioning processes which render the air often disagreeable for the respiratory organs or what is colloquially known as "dead". For this reason one is inclined to wonder whether the designing of elaborate apparatus for determining comfort temperatures is advisable until an answer is given to the much more important question of what causes air to feel "dead". If conditions in a room are such that the air movement is small, the temperature around 66° F. so that humidity is not of great importance, and with no strong sources of heat radiation present, the work described points to the possibility that two thermometers placed at head level and at foot level will give a fair indication of whether the room is comfortable.

Since the beginning of this work the eupatheoscope Mark II (3) has been developed, but as the general principle upon which it operates is similar to that of the eupatheoscope discussed in this note, it is not considered probable that, by having substituted it for the eupatheoscope used by the writer, very different conclusions would have been reached.

The "Rutledge Pure Air" System

After the completion of the observations on the eupatheoscope, a system developed by R. Rutledge, called the "Rutledge Pure Air", was examined to observe its effect on the freshness of the air in a room. Some measurements were made on the temperature gradient and the relative humidity in the room containing the installation, as well as in two other rooms for comparison. Owing to the fact already mentioned, that the temperature gradient has a bearing on "comfort" temperature, a description of this work and the results are given.

The Rutledge system consists in placing shallow pans very close to the ceiling and circulating water through them. In this way a very large surface of fresh water is exposed to the air of the room at the very part where warm vitiated air collects. The system was not devised primarily for occupied rooms but for cold stores, and it is claimed that in a cold store where it is installed products such as meat keep in much better condition than in ordinary cold stores. If this statement be correct, it is reasonable to suppose that the system should keep the air of a room fresher. The installation of the pans over about half the area of the ceiling of the room in which the work on the eupatheoscope was carried out has had very noticeable effects. Non-technical visitors to the room have remarked that they noticed the difference at once when they entered. One visitor remarked that it felt quite "exhilarating".

To give a scientific explanation of this is not easy; several possibilities suggest themselves. The first is that the humidity was higher; but then in reply to this suggestion one may argue that the very best humidifying systems in air-conditioned houses do not necessarily give the exhilarating feeling but sometimes the reverse. A second suggestion is that the cold water circulating overhead reduced the temperature gradient. Evidence to this effect has been found, and is presented in Tables III, IV and V. But it is not entirely conclusive. A third suggestion is that by humidifying the air in the room a lower temperature was found comfortable. A fourth suggestion is that radiation was taking place from the subject to these cold pans, and as the head was nearer to the pans than were the feet the effect was somewhat similar to an inversion of the ordinary temperature gradient. Thermometers hung in the air would not have registered this effect. A fifth suggestion is that the effect was due to some phenomenon not as yet understood, but connected with the passing of air over moving water. Mr. Rutledge himself favors this idea.

The fact remains, however, that whatever the cause may be, the effect was present. The room A, in which the pans were installed, was compared with two other rooms. One of these, B, was next to it in the building and was therefore exposed to similar winds, while the other, C, was on the other side of the building. The radiator in C was kept on all the time, but in A and B it had to be turned off at times and the windows opened. In room A, the temperature at 9 a.m. was usually intolerably warm, and the plan was adopted of

TABLE III
Room *A*

Date	Outdoor temp., °F.	Temp. on floor, °F.	Temp. at head, °F.	Temp. at ceiling, °F.	Head-floor, °F.	Ceiling-floor, °F.	Rel. hum., %	Remarks
Jan. 28	8	71	72.3	74.7	1.3	3.7	61	Radiator on overnight
Jan. 29	26	70.4	71.3	72.5	0.9	2.1	66	Radiator on overnight
Feb. 2	7	65	67.1	68	2.1	3.0	45	Radiator on overnight
Feb. 3	6	67	69.3	71	2.3	4.0	44	Radiator on overnight
Feb. 4	10	71.5	73.5	75.5	2.0	4.0	54	Radiator on overnight
Feb. 5	20	73	74.3	76.3	1.3	3.3	62	Radiator on overnight
Jan. 27	0	63	64.3	64	1.3	1.0	54	Radiator off overnight
Jan. 30	18	62.3	62.6	63.4	0.3	1.1	55	Radiator off overnight
Feb. 1	30	60	60.1	60.2	0.1	0.2	58	Radiator off overnight
Jan. 27		65.5	67.8	70	2.3	4.5		1 hr. after radiator turned on
Jan. 27		66.5	69.3	71	2.8	4.5		2 hr. after radiator turned on
Jan. 27		65.2	66.3	67	1.1	1.8		1 hr. after radiator turned off
Jan. 28		71	71.3	71.9	0.3	0.9		½ hr. after radiator turned off
Jan. 28		66.7	68.5	70	1.8	3.3		Radiator off and window opened 2 in.
Jan. 28		61	66.3	67	5.3	6.0		Window opened wide; then closed
Jan. 28		65.5	66.2	67.9	0.7	2.4		40 min. later
Feb. 2		59.2	61.3	62.4	2.1	3.2		Radiator off; afternoon readings
Feb. 3		63.5	64.3	65.1	0.8	1.6		Radiator off; afternoon readings
Feb. 4		67.5	67.5	68.1	0	0.6		Radiator off; afternoon readings

TABLE IV
Room *B*

Date	Outdoor temp., °F.	Temp. on floor, °F.	Temp. at head, °F.	Temp. at ceiling, °F.	Head-floor, °F.	Ceiling-floor, °F.	Rel. hum., %	Remarks
Jan. 27	0	65.7	69.5	74.4	3.8	8.7	19	Radiator on overnight
Jan. 28	8	67.5	71	74.2	3.5	6.7	16	Radiator on overnight
Jan. 29	26	68.7	72	74.2	3.3	5.5	20	Radiator on overnight
Feb. 2	7	60.7	65.2	68.2	4.5	7.5	15	Radiator on overnight
Feb. 3	6	64.9	68	70.2	3.1	5.3	15	Radiator on overnight
Feb. 4	10	70.2	74.5	77.5	4.3	7.3	18	Radiator on overnight
Feb. 5	20	72.5	75.5	79.4	3.0	6.9	24	Radiator on overnight
Jan. 30	18	62.7	64.5	67.2	1.8	4.5	25	Radiator off overnight
Feb. 1	30	60.7	62.5	64.7	1.8	4.0	24	Radiator off overnight

TABLE V
Room *C*

Date	Outdoor temp., °F.	Temp. on floor, °F.	Temp. at head, °F.	Temp. at ceiling, °F.	Head-floor, °F.	Ceiling-floor, °F.	Rel. hum., %	Remarks
Jan. 27	0	72.5	75.7	81.4	3.2	8.9	22	Radiator on overnight
Jan. 28	8	71.6	75.1	78.9	3.5	7.3	15	Radiator on overnight
Jan. 29	26	67.8	71.8	75.9	4.0	8.1	15	Radiator on overnight
Jan. 30	18	68.7	74	79.6	5.3	10.9	14	Radiator on overnight
Feb. 1	30	68.7	70	72.9	1.3	4.2	20	Radiator on overnight
Feb. 2	7	70.2	72	76.3	1.8	6.1	15	Radiator on overnight
Feb. 3	6	71.4	76	80.9	4.6	9.5	10	Radiator on overnight
Feb. 4	10	74.5	76.8	81.4	2.3	6.9	10	Radiator on overnight
Feb. 5	20	70.8	73.2	77.4	2.4	6.6	13	Radiator on overnight

cooling off the room, turning off the radiator and allowing the temperatures to adjust themselves. Readings were taken in the afternoon. On the three occasions on which the radiator was off overnight in room *A*, low gradients were found in the morning. So many factors enter into a full discussion of these data that it is unwise to draw too definite conclusions from them, but the general impression is given that the temperature gradient was smaller in room *A* than in either of the others. The temperature difference between the head and the feet of a sedentary worker was about twice in the one case what it was in the other; furthermore, the relative humidity in room *A* was about three or four times as high as in *B* or *C*. From Table III it is clear that keeping the radiator on, increased the temperature gradient. Since opening a window introduces a cold layer of air on the floor of a room, the conventional practice of keeping the window open and the radiator on creates a large temperature gradient, and therefore, according to both Hill and Angus, keeps the room uncomfortable. It is clear that further investigation along these lines should be carried out.

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THE EFFECT OF REGAIN ON THE RATE OF ADSORPTION OF STANNIC CHLORIDE BY SILK FIBROIN[1]

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Abstract

The effect of the moisture content of silk fibroin on the amount of weighting it takes up in given periods of time from a 30° Bé. stannic chloride solution has been determined. Saturated silk (>35% moisture content) attains maximum adsorption much faster than does dry silk, whereas a minimum rate of adsorption exists for silk of about 10–23% moisture content. An explanation has been advanced for these phenomena based on the rate of swelling of silk in water and in stannic chloride solution, the size of the pores in dry silk and the effect that the water in these pores would have on the stannic chloride solution entering them. It is pointed out that the weighting taken up by silk from stannic chloride solutions is probably adsorbed not as stannic chloride but as a mixture of the various tin complexes which have been shown to exist in aqueous stannic chloride solutions. The effect on the weighting of increasing the temperature of the hydrolyzing bath and of the addition of inorganic chlorides and sulphates to this bath has also been investigated. The final weighting retained by the silk has been shown to consist of hydrated stannic oxide, the amount of water present depending upon the conditions obtaining during hydrolysis and drying.

Introduction

The loading of silk with tin—the process consisting of soaking the silk in stannic chloride solution, followed by a hydrolysis with water and treatment with disodium phosphate—is a practice of considerable importance in the silk finishing industry, where the process is known as "weighting". The treatment can be repeated until the desired weighting is attained. Coughlin (5) has shown that the process consists of an apolar adsorption of stannic chloride molecules by the silk, and Chinn and Phelps (4) have demonstrated that it is a negative adsorption in the region of concentrations of stannic chloride most commonly used in the industry.

The work described here deals with the first phase of commercial weighting, *viz.*, the adsorption of stannic chloride* by the silk and its hydrolysis, in the fibre, to hydrated stannic oxide, and specifically with the effect which the moisture content or "regain" of the silk has on its rate of adsorption of the stannic chloride.

* *The probability that other tin complexes, rather than stannic chloride, are adsorbed, is pointed out in the body of the paper. However, for the sake of convenience, the term stannic chloride will be used when adsorption by silk from stannic chloride solutions is discussed, but it will be understood to refer to whatever tin complexes the silk actually does adsorb.*

The sericin or "silk gum" was removed from the silk by treatment with hot soap solution. The silk fibroin, which is unaffected by this process, was thus obtained in a pure state. Samples of this "degummed" silk of known dry weight were then brought to the desired moisture content, at a thermostatically controlled temperature, in a suitable humidifying chamber. This process is known to the trade as "conditioning". The samples were then reweighed and immersed in a stannic chloride solution of 30° Bé. (362 gm. per litre) for various periods of time, hydrolyzed in distilled water, dried and weighed again.

Then

$$\frac{\text{(conditioned weight } - \text{ original dry weight)} \times 100}{\text{original dry weight}} = \text{percentage regain,}$$

and

$$\frac{\text{(final dry weight } - \text{ original dry weight)} \times 100}{\text{original dry weight}} = \text{percentage weighting.}$$

Experimental

Preparation of Samples

The silk used was a loosely woven flat crêpe of Japanese origin. It was carefully degummed at 98–100° C. in two successive soap baths containing 1 and 0.5% of soap respectively, and after several hot water rinses it was freed from the last traces of soap by extraction with 70% alcohol. The residual alcohol was removed with boiling distilled water. The silk was then adjusted to a pH of about 4, (the most acceptable value for its isoelectric point (6)), by allowing it to reach equilibrium with a solution of hydrochloric acid maintained at this pH by the necessary additions of dilute hydrochloric acid.

After the silk was air-dried, it was cut into 0.8–1.0 gm. samples which were individually dried and weighed. These were then conditioned for two months in desiccators containing saturated salt solutions of known vapor pressure, the desiccators being stored in an air thermostat at 20° C. ± 0.1°. After the samples were weighed to determine their regains, they were ready for weighting. The solutions used for conditioning are listed in Table I, together with the approximate relative humidity produced (10, p. 67; 20, p. 1273; 25, p. 328) and the regain attained by the samples in each case.

TABLE I

Solution	Approx. rel. hum. produced, %	Regain attained, % of wt. of dry silk
$KC_2H_3O_2$	20	4.1
$Na_2Cr_2O_7 \cdot 2H_2O$	52	8.0
K_2CrO_4	88	14.1
$NH_4H_2PO_4$	93	17.0
K_2SO_4	96	19.1
H_2SO_4 (d, 1.05)	97	21.7
H_2SO_4 (d, 1.045)	97.5	22.5
H_2SO_4 (d, 1.025)	99	25.7

Weighting and Hydrolysis

A freshly prepared c.p. stannic chloride solution of 30° Bé. was used for the weighting solution, as this is the strength generally employed in the industry. The weighting was done in a one litre beaker, the stannic chloride

solution being stirred gently by means of an automatic stirrer, and maintained at 20° C. ± 1° in a water bath. The samples were plunged into this solution on removal from the weighing bottles. After the required period of immersion they were transferred to a large volume of distilled water maintained at 20° C. where the stannic chloride which they had adsorbed was hydrolyzed, and thus fixed on the fibre as a hydrated stannic oxide $SnO_2 . xH_2O$ (17, pp. 407-410; 24, p. 187) as will be discussed below. After 20 to 30 min. in the distilled water the samples were rinsed under running tap water, dried and weighed. The main series of weightings (Fig. 2) were all completed within one week, too short a period for the stannic chloride to change its state of hydrolysis appreciably during the course of the experiments (7; 13, p. 273). That the age of a stannic chloride solution does affect its rate of adsorption by silk is shown below.

Weightings were also performed with bone-dry and wringing-wet samples. The latter were soaked in distilled water overnight and then wrung out well before immersion in the stannic chloride bath. The amount of water that the silk will adsorb under these conditions should correspond to that which it will take up from a saturated atmosphere, viz., 35% at 20° C. (3). The amount adsorbed will probably be slightly greater than this, as Katz (12) indicated. However, the actual equilibrium moisture content is of no great importance for the purposes of this paper, since excess water always adhered to the samples after they were wrung out. Hence the results for the wet samples were plotted on the graphs as corresponding to a regain of 35%.

Results

Fig. 1 shows the results obtained when this investigation was started (11). A weighting period of one hour was used. It was thought, at first, that the graph represented equilibrium conditions, with a distinct minimum weighting of 5% occurring for silk of 19% regain, since dry silk requires only 10–15 min. to attain maximum adsorption of stannic chloride, as Coughlin (5) has shown. However, samples of 19.1% moisture content were weighted for two hours, and they took up an average of 9.3% weighting, so that it became obvious
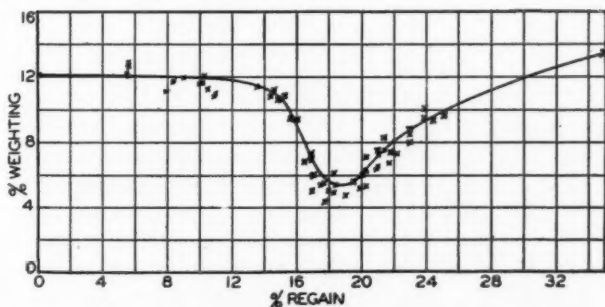

FIG. 1. Graph showing relation between moisture content of silk and weighting taken up during a one hour immersion in 30° Bé. stannic chloride solution.

that the regain of the silk affected the rate of its adsorption of stannic chloride, and did not affect the actual amount of adsorption at equilibrium.   Accordingly, a more elaborate series of experiments were carried out when this work was resumed in 1934–35, the results of which are shown in Fig. 2.   Here
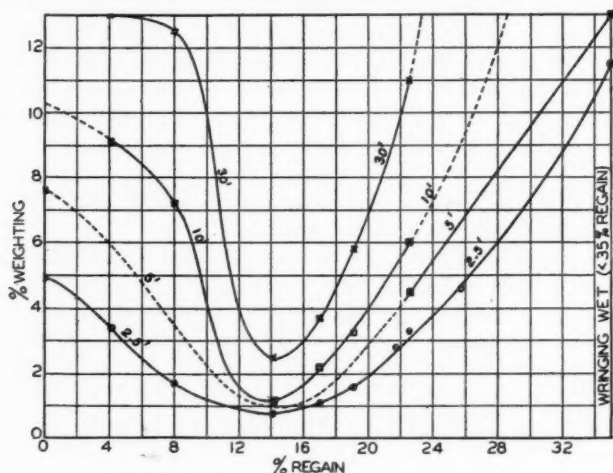

FIG. 2.   *Graph showing effect of regain on weighting taken up by silk during various periods of immersion in 30° Bé. stannic chloride solution.*

TABLE II
RELATIVE WEIGHTINGS

Low weighting 2.5 min.	Medium weighting 10 min.	High weighting 30 min.
%	%	%
1.91	6.82	12.8
1.55	7.44	12.6
1.62	7.38	12.4
1.69	6.97	12.1
Av. 1.7	Av. 7.2	Av. 12.5

each point gives the average of four determinations.   Points representing equal periods of immersion of the samples in the stannic chloride bath were joined by continuous lines.   The usual variation in the results obtained for four separate samples is given in Table II.   The figures are for the experiment in which the regain was 8%.

The maximum weighting obtained under the conditions described above was $13.1\% \pm 0.3$.

Discussion of Results

It is apparent that there is a great variation in the rates of adsorption of stannic chloride by silk samples of different moisture content.   It is rather surprising that samples saturated with water adsorb stannic chloride much faster than dry samples, and still more difficult of explanation is the fact that samples approximately half saturated with water adsorb the least amount of stannic chloride in a given period of time.   The exact position of the minimum amount of adsorption on the regain base seems to vary slightly. It depends on the nature and history of the silk and also on the time during

which the silk remains immersed in the stannic chloride solution. This is clearly shown in Fig. 3, where the results obtained by Press (18) with Chinese silk are graphically represented. It is seen that samples of 13, 17.5 and 23.8% regain all attained equilibrium in about the same time, *viz.*, 110 min., but
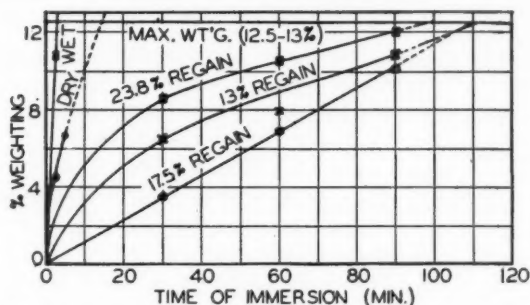

FIG. 3. *Graph showing variation in weighting with time, for silk of various moisture contents immersed in 30° Bé stannic chloride solution.*

that the weighting after 30 min. immersion was much less for the samples of 17.5% regain than for the other two sets. However, two facts stand out clearly, *viz.*, (1) saturated silk adsorbs stannic chloride much faster than does dry silk, and (2) silk of about 10–23% moisture content adsorbs stannic chloride much more slowly than even dry silk does. These phenomena are discussed below.

Discussion of Results for Dry and Saturated Silk

Since silk in a saturated and (consequently) swollen condition attained maximum adsorption of stannic chloride in less than five minutes, it is obvious that the rate of diffusion of the stannic chloride molecules into the porous network of the fibre is very rapid when the pores are enlarged, as they are in a saturated fibre. (For a complete discussion on fibre structure, swelling during water sorption, etc. see (2, 1, 15, 16, 22).) It will be sufficient to state here that the pores or intermicellar spaces in a fibre increase in size as the fibre swells during water sorption, and not the micelles themselves. Hence stannic chloride molecules must enter these pores and be adsorbed on the pore walls. On hydrolysis the resulting coagulated precipitate of $SnO_2 \cdot xH_2O$ is left mechanically trapped in the intermicellar spaces, and the active groups in the silk are free to adsorb fresh stannic chloride molecules. Herzog and Conell (9) have shown that the X-ray photograph of the fibre of silk is not changed by weightings as high as 50 to 65%.

It seems probable that the factor which determines the time required for dry silk to attain maximum adsorption of stannic chloride is the rate of swelling of the silk in the stannic chloride solution, whereby its porous structure is made accessible to the stannic chloride molecules. To test this hypothesis, experiments were performed on the rate of swelling of silk gut in water and stannic chloride solution and on the rate of adsorption of stannic chloride by

dry and saturated gut. Silk gut (as prepared for surgical sutures) was used in preference to individual silk fibres because it could be handled much more conveniently. The silk gut is prepared by dissecting out the silk sac of the silk worm and extending the sac (15). The gut consequently consists of pure silk fibroin free from sericin. The experimental technique and results are given below.

It is of interest at this point to compare the average diameter of the pores in dry silk with that of the stannic chloride molecule. It has been found in this laboratory, that methyl and ethyl alcohols will swell dry silk gut, but that propyl or butyl alcohol will not*. It appears reasonably safe, therefore, to conclude that the pores in dry silk are too small to admit propyl alcohol and that their diameter is somewhat less than 6 Å. (Speakman (22) has found that the pores in dry wool admit the propyl alcohol molecule, and he places their diameter at 6 Å.)

The diameter of the stannic chloride molecule, calculated from its parachor as given by Sugden (23, p. 187), is about 6.5 Å. If it is assumed that the structure of silk fibre is the same as that of silk fibroin in gut form, it seems fairly certain that silk must swell to a certain extent before the pores are large enough to admit stannic chloride molecules. The same conclusion would apply to other tin complexes such as $SnCl_3OH$, H_2SnCl_6, etc. (see below), since these will in general have a molecular diameter as great as, if not greater than, that of the stannic chloride molecule.

Experiments with Silk Gut

Silk gut of diameter about 0.4 mm. was employed in the following experiments. It was washed in benzene and then in boiling water to remove surface grease and impurities before use. Samples weighing about 0.2 gm. were then weighted, at a temperature of 25° C., both in a bone-dry and in a water-saturated condition as described. Hydrolysis was allowed to proceed for 24 hr. to ensure completion. The results are shown in Table III.

TABLE III
RESULTS OF WEIGHTING SILK GUT

Period of of immersion in stannic chloride, hr.	Dry samples, % weighting	Wet samples, % weighting
0.5	0	–
6	2.2	7.9, 9.4
9.5	3.6, 3.5	–
15	4.8, 5.2	–
19.5	5.2	9.5, 12.7
48	11.3, 11.7	–
67	12.4	–

Although the results are somewhat irregular it is obvious that silk gut behaves in a manner analogous to the behavior of silk fibre in crêpe form, in that saturated samples adsorb stannic chloride much faster than do dry samples. The swelling of silk gut in stannic chloride (30° Bé.) and in distilled water at 25° C. was next determined. Photographs of

* *Details of this work will be included in a paper that the writers hope to publish in the near future.*

four samples of gut held vertically by wire supports in a small rectangular plane glass cell were taken, and the diameters of the fibre images on the photographic plates were measured with a traveling microscope. The camera produced a magnification of about two diameters. The true fibre diameter could be obtained by means of the image of a platinum wire of known diameter placed alongside the fibres in the cell. The fibres could be rotated, each about its own vertical axis. Since the gut samples were all slightly elliptical in cross section, two photographs were always taken for each determination of diameter, the fibres being rotated through an angle of 90° for the second exposure. The geometrical mean of the two figures obtained for the average diameter of any one fibre from the two plates was then taken as the mean fibre diameter. The average diameter was the arithmetical average of 10 measurements made at equally spaced intervals along the fibre length. Photographs were first taken of the dry fibres (in air) and then at various intervals of time after the swelling liquids had been poured into the cells. The results are given in Table IV.

TABLE IV

SWELLING OF SILK GUT

Time in liquid, hr.	Average lateral increase in diameter of gut samples	
	Water, %	Stannic chloride, %
6	20	11
24	21 ± 2	14
72	—	22 ± 2

These figures are slightly higher than those obtained by Lloyd and Marriott (15) (16 to 18%) for the equilibrium lateral swelling of silk gut in water and in 1 N hydrochloric acid. However, the figures represent the relative rates of swelling sufficiently accurately for our purpose, and they clearly show that silk gut swells much more rapidly in water than in stannic chloride solution, although at equilibrium the percentage of swelling is about the same in both liquids.

Furthermore, saturated silk gut attains maximum adsorption of stannic chloride in 24 hr. or less, whereas dry gut swells only to $\frac{14 \times 100}{22} = 64\%$ of its final value in this time. The assumption made that the rate of swelling of dry silk in the stannic chloride solution governs its rate of adsorption of stannic chloride is thus proved to be correct.

Discussion of the Minimum Rate of Adsorption

There is still left to be explained the minimum rate of adsorption of stannic chloride observed for silk which is only about half saturated with moisture (10 to 23% regain). The chief reason that dry silk swells more slowly in stannic chloride solution than in water must be due to the blocking effect that the molecules of stannic chloride produce in the intermicellar channels as they are adsorbed on the surfaces of the micelles. (The decrease in the concentration of water molecules in stannic chloride solution of 30° Bé. (1.39 moles per litre) is only about 16%). Thus the diffusion of succeeding water (and stannic chloride) molecules into the pores is hindered and the silk swells much more slowly.

Following this line of reasoning it is apparent that the pores in silk of
10 to 23% moisture content must be more immediately and more effectively
blocked by adsorbed stannic chloride molecules than is the case with dry
silk. That is to say, the water in the pores catalyses the adsorption of stannic
chloride in some way, so that the stannic chloride molecules that first enter
the pore openings are immediately adsorbed and thus greatly hinder the
inward diffusion of succeeding water or stannic chloride molecules. The
result is that the silk swells much more slowly, and consequently requires
a much longer time to attain maximum weighting. Obviously, as the moisture
content of the silk is increased beyond this critical point, the pores become
larger and are not so readily blocked, so that the rate of adsorption of stannic
chloride increases with the moisture content and reaches a maximum for
completely saturated silk.

The only apparent effect that the water in the silk pores could have on the
stannic chloride would be to increase its degree of hydrolysis. The hydrolysis
occurring in aqueous stannic chloride solutions is discussed below. The
experiments described in the following paragraph were devised to ascertain
whether stannic chloride is actually adsorbed more rapidly by silk when its
degree of hydrolysis is increased.

Adsorption from Diluted and Aged Stannic Chloride Solutions

The two obvious methods of increasing the hydrolysis of the standard
stannic chloride solution used in the above-mentioned experiments were to
dilute it and to age it. Accordingly a fresh 30° Bé. stannic chloride solution
(362 gm. per litre) was made up as a reference solution and part of it was
diluted to 22° Bé. (245 gm. per litre). Another 30° Bé. stannic chloride
solution, which was about five months old, was used as the aged solution.
Samples of Chinese silk crêpe were prepared exactly as before (the supply
of Japanese silk had been exhausted and no more could be obtained at the
time), and weighted in the above-mentioned solutions both in the dry and
water-saturated condition for various periods of time as shown in Table V.

TABLE V

EFFECT ON WEIGHTING OF AGING AND DILUTING THE 30° BÉ. STANNIC CHLORIDE SOLUTION

Condition of samples before weighting	Time of immersion in stannic chloride solution, min.	% weighting		
		Fresh 30° Bé. solution	Aged 30° Bé. solution	Fresh 22° Bé. solution
Dry	2.5	5.8	7.6	8.3
Dry	5.0	—	—	9.8
Wet	1.0	8.7	8.8	8.6
Wet	2.5	12.1	—	9.3
Wet	60.0	13.2	13.1	9.8

The pH of the fresh 30° Bé. solution was 0.46, that of the aged, owing to
slow hydrolysis, was 0.23. It is seen that in 2.5 min. dry silk picks up
5.8% of weighting from the fresh solution, compared with 7.6% from the

aged solution and 8.3% from a much more dilute solution, although the last result is undoubtedly partly accounted for by the fact that the silk would swell more rapidly in the more dilute solution. Little difference can be noted in the results for saturated silk in the two concentrated solutions. It is rather remarkable that silk in this condition picks up virtually as much weighting in one minute from a 22° Bé. solution as it does from a much more concentrated solution, since, in this case, the "swelling" factor is completely eliminated. These results show conclusively that, other conditions being equal, the rate of adsorption of stannic chloride by silk fibroin increases with the degree of hydrolysis of the stannic chloride solution.

Hydrolysis of Stannic Chloride Solutions

It has been tacitly assumed above that silk adsorbs tin from stannic chloride solutions as stannic chloride, since Coughlin found that the ratio of tin to chlorine in the weighting bath does not change. However, this is still an assumption, since no investigator has been able to confirm the presence of any appreciable quantity of stannic chloride in its aqueous solutions (8,21). The hydrolysis of stannic chloride solutions has been investigated by Foster (7), Carstanyen (17, p. 440), Kohlrausch (13, p. 273) and von Kowalewsky (14) and more recently by L. Smith (21), Milda Prytz (19) and Guéron (8). The work of these investigators shows that the rate of hydrolysis of these solutions increases rapidly with dilution and temperature, but is very slow in a solution of the concentration employed by us. However, no completely satisfactory mechanism for the hydrolysis is suggested. It is generally agreed that tin exists in the solution as a complex anion or cation or both. The solutions, of course, are all acid owing to partial hydrolysis, and Smith finds that fresh concentrated solutions contain more Cl^- ions than H^+ ions, which tends to show the presence of positive tin complexes. Guéron concludes, from studies of Raman spectra, that solutions more concentrated than 0.5 molar contain very few molecules of stannic chloride but large numbers of $SnCl_6^{--}$ ions as well as positive tin ions such as Sn^{++++}, $SnCl_3^+$, $SnCl_3OH$, $SnCl_2OH^+$ etc. Milda Prytz finds, from potential measurements in dilute solutions (0.01 to 0.1 molar), that the number of Sn^{++++} ions present varies directly with the concentration of stannic chloride when the Cl^- concentration is kept constant, and that, accordingly, no complex exists containing more than one tin atom. Guéron, on the other hand, considers that $SnCl_6^{--}$ ions can be formed in two ways, *viz.*

$$(1) \quad 3\,SnCl_4 \longrightarrow Sn(SnCl_6)_2$$
$$(2) \quad 3\,SnCl_4 + 2\,H_2O \longrightarrow SnO_2 + 2\,H_2SnCl_6$$
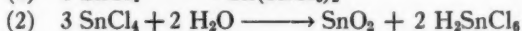
It is impossible, at present, to reconcile these results and theories with the fact that neither the tin-to-chlorine ratio nor the pH of a stannic chloride solution changes during weighting. The specific adsorption of any one tin complex by the silk, except stannic chloride (or a polymer thereof, *e.g.* $Sn(SnCl_6)_2$) would obviously upset the original tin-to-chlorine ratio in the

main body of the weighting solution.   Hence, we must conclude from existing evidence that if stannic chloride or $Sn(SnCl_6)_2$ does not exist in appreciable concentration in aqueous stannic chloride solutions, a mixed adsorption of various complexes such as $SnCl_4$, $SnCl_3OH$, $SnCl_2OH^+$, $SnCl_6^{--}$, H_2SnCl_6, $SnCl_5OH^{--}$, etc. must result in a purely fortuitous removal of SnCl from the weighting solution in the approximate ratio of Sn:4 Cl.

The fact that concentrated solutions of stannic chloride contain large quantities of $SnCl_6^{--}$ ions may well explain the shift from positive to negative adsorption of tin that silk exhibits (4), as the concentration of the stannic chloride solution is increased.   If $SnCl_6^{--}$ is not adsorbed (or is negatively adsorbed) by silk, and the concentration of $SnCl_6^{--}$ increases at the expense of other tin complexes as the concentration of the stannic chloride is increased in an aqueous solution (which seems evident from Guéron's work), then it would be expected that silk would show a maximum adsorption at some particular concentration of stannic chloride and decreasing adsorption on either side of this critical concentration.

Effect of Temperature and Various Salts on Hydrolysis

In concluding this paper the results of some experiments will be presented which show how various changes in the conditions of hydrolysis affect the weighting retained by silk.

Since the hydrolysis of stannic chloride is hastened both by increase of temperature and the addition of coagulating salts (8) and retarded by hydrochloric acid, and sodium and potassium chlorides, it was decided to find out what effect these factors would have when applied to the hydrolysis of the stannic chloride adsorbed by silk which had come to equilibrium with a stannic chloride solution of 30° Bé.

Saturated samples of Chinese silk crêpe were weighted in the usual manner, hydrolyzed in duplicate under different conditions as specified below, then rinsed well under running tap water and finally dried and weighed.   The stannic oxide in the samples was determined by igniting them to constant weight and subtracting the ash of the silk itself.   Then,

$$\frac{\text{corrected weight of ash} \times 100}{\text{dry weight of original sample}} = \text{percentage stannic oxide in sample.}$$

The difference between the percentage weighting and the percentage stannic oxide in a sample represents the water present.   This is expressed in Table V as a percentage of the total weighting.   Thus

$$\frac{(\text{percentage weighting} - \text{percentage stannic oxide}) \times 100}{\text{percentage weighting}} = \text{percentage water in the weighting.}$$

The complete results are tabulated in Table VI.

TABLE VI

EFFECT OF VARIATIONS IN THE CONDITIONS OF HYDROLYSIS

Conditions of hydrolysis	% weighting in samples	% stannic oxide in samples	% water in weighting
Distilled H_2O at 25° C.	12.7	–	–
Distilled H_2O at 100° C.	11.4	–	–
Distilled H_2O at 25° C.	13.9	13.0	6.5
Distilled H_2O at 85° C.	13.6, 11.5	12.7, 10.6	6.6, 7.8
Distilled H_2O at 100° C.	11.5, 11.3	10.8, 10.8	6.1, 4.4
$\frac{1}{15}N$ Na_2SO_4 solution	16.8, 16.0	–	–
$\frac{1}{15}N$ $(NH_4)_2SO_4$ solution	16.4	14.8	9.8
$\frac{1}{15}N$ $ZnSO_4$ solution	15.4	14.0	9.1
10% solution $CaCl_2$	7.5, 6.3	–	–
10% solution KCl	5.7, 5.1	–	–

It is seen that an increase in the temperature of the hydrolyzing bath decreases slightly the stannic oxide retained by the silk, although the rate of hydrolysis of the stannic chloride solution adhering to the samples is greatly increased, as shown by the precipitate of stannic oxide which appears immediately when the samples are plunged into the hot water. Evidently the increased swelling and increased rates of diffusion of the various tin complexes at the higher temperature more than counteract the influence that this increased rate of hydrolysis would be expected to exert, *i.e.*, to cause more tin to be entrapped in the silk pores as stannic oxide and thus produce a higher weighting.

The salts that retard or repress the hydrolysis of stannic chloride, *viz.*, sodium chloride, potassium chloride and calcium chloride, produce a lower weighting when added to the hydrolyzing bath, as would be expected. Furthermore, those salts which cause coagulation and precipitation of dilute stannic chloride solutions (*i.e.* of a positively charged stannic oxide sol (Guéron, Weiser)) produce a weighting higher than normal, as would be expected, since the stannic oxide particles have less time to diffuse out of the silk pores before they are coagulated and precipitated.

The percentage stannic oxide in weighted silk is seen to be always less than the percentage weighting, as has been noted by Coughlin and by Chinn and Phelps (4). They considered the difference to be due to water adsorbed by the silk, but it is obvious that it is water adsorbed by the stannic oxide retained in the silk pores which cannot be driven off by heating at 100° C. Thus L. Schaffner (24, pp. 202, 203, 213-215) found that the α-oxide retains 8% of water at 100° C. and the β-oxide about 12%. The values obtained by the writers are of the same order of magnitude as these figures. The samples hydrolyzed at 100° C. would be expected to have the lowest water content, since Weiser shows that the β-oxide is formed by the hydrolysis of stannic chloride at elevated temperatures. The stannic oxide precipitated in the pores with the aid of the coagulating SO_4^{--} ion retained the greatest amount of water.

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THE DETERMINATION OF SULPHUR IN WOOL[1]

By P. Larose[2] and A. S. Tweedie[3]

Abstract

A modification of Pregl's micromethod for the determination of sulphur in organic compounds has been found to be satisfactory and convenient when applied on a macro scale to wool.

The investigation of various methods of cleaning the samples shows that the best results are obtained when the wool wax is extracted with a solvent before washing with water. It is shown that a treatment with dilute hydrochloric acid is not necessary in preparing the sample.

Three different procedures have been followed in determining the dry weight of the sample and the differences in the results are discussed. Results obtained by the new method are compared with those obtained by other recognized methods, and the agreement with the results of the Benedict-Denis-Barritt method is shown to be very good.

Introduction

The predominant role of sulphur in wool is shown clearly by the work of Astbury, Speakman and others. Some of the physical and chemical properties of wool have been attributed to its sulphur content. In view of this the determination of sulphur in wool is important. A number of methods have been proposed and employed for this determination. Although the results obtained by the use of some of these methods are claimed to be satisfactory, the writers wish to describe a new method that has certain advantages over the others.

Method

The method is a modification of Pregl's method for the microdetermination of sulphur in organic compounds. It was developed in 1926 by A. Cambron, of the National Research Laboratories, Ottawa, for the determination of sulphur in organic compounds such as the xanthates. The Pregl method was tried on a macro scale and found unsatisfactory for these compounds, and the modifications described here had to be made before satisfactory results could be obtained. It was suggested that Cambron's method might be a convenient one for determining sulphur in wool. Preliminary experiments made in 1931 showed that the method was satisfactory for this purpose, but the results obtained at that time were too meagre to warrant publication. During the past year a number of determinations were made with this method, and a number of the samples were also analyzed by the Carius and the Benedict-Denis methods for the purpose of comparison.

The method consists essentially in burning the material in a stream of oxygen, passing the products of combustion over platinum and absorbing them in hydrogen peroxide solution. The sulphur was determined as barium sulphate in the usual way.

The apparatus used is shown schematically in Fig. 1. E is a quartz tube 24 in. long*. A portion of its length is heated in a furnace, F. H and K are the platinum catalysts which oxidize the sulphur dioxide to sulphur trioxide. H is the platinum contact star of a standard type for combustion tubes. K is a roll of platinum gauze.
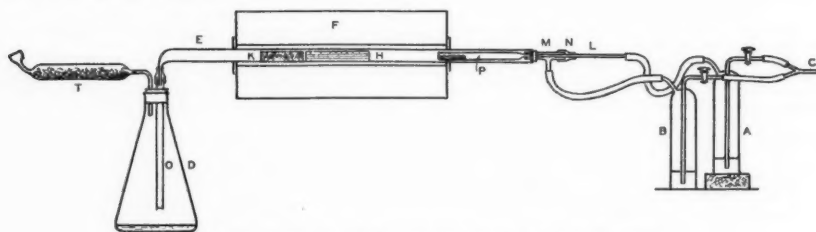

FIG. 1. *Apparatus for the determination of sulphur in wool.*

One end of the quartz tube is sealed to a small tube at right angles to it. This small tube fits into a somewhat larger delivery tube, O, that passes through the cork of the absorption flask, D. The two tubes are held together by a short piece of rubber tubing. To the absorption flask, D, is connected a tube, T, filled with small pieces of glass rod; 25 cc. of 5% hydrogen peroxide is placed in the flask, and 5 cc. in the tube T so as to wet thoroughly the small pieces of glass. The end of the tube O is adjusted to a height of about one inch above the surface of the liquid.

The sample of wool is placed in the quartz tube, P, of a diameter slightly smaller than that of the tube E. Tube P is sealed to a tube L of smaller diameter. A tube M, concentric with L, is joined to L by means of a short length of rubber tubing, N. Both tubes pass through the cork closing the end of the tube E. M carries a side tube connected to a bubbler, B, while L is connected to the bubbler A. A stream of oxygen is introduced at C. It passes through the bubblers and enters the combustion tube through the tube P and through the annular space between M and L. The purpose of the bubblers A and B (containing water) is to permit adjustment of the gas stream in both inner and outer tubes. During combustion the gas is bubbled through A at a rate of about one bubble every two seconds, while that through B is slightly more rapid.

The purpose of the outer stream is to prevent any back flow of the products of combustion, some of which are liable to cause an explosion if combustion is rapid. This arrangement and that of the absorption flask are the modifications made to Pregl's apparatus. Because of these modifications the sulphur trioxide collects as a cloud over the surface of the solution and is slowly absorbed by it. The tube T insures complete absorption.

At the beginning of a determination, the furnace is heated and when the temperature at the centre is 650° C. the wool sample, wound with a short piece of platinum wire to keep it in a fairly compact roll, is introduced into the end

* *As the apparatus was drawn to scale, the dimensions of the other parts can readily be estimated.*

of the tube P, which is then adjusted so that its end is just inside the furnace. As the wool burns, the tube L is gradually pushed forward until the tube P is virtually in contact with the platinum H.   The wool is entirely carbonized after about 20 min. in the combustion tube.   The combustion is continued for a further 20 min.   This is usually sufficient to burn off the carbon completely. Only a small amount of ash is left in tube P.   The quartz tube, E, is then disconnected at its inlet end, the furnace is opened and the tube is taken out to cool.   Care must be taken during this manipulation that any condensed acid in the cool part of the tube does not run back into the heated section and vaporize.   When the tube has cooled sufficiently, it is washed with distilled water and the washings are run into the flask D.   The contents of the tube T is also washed carefully into D.   Then the solution is boiled to decompose the hydrogen peroxide and to reduce the volume of liquid.   The ash remaining in the tube P is washed into a beaker and heated with dilute hydrochloric acid to dissolve as much of it as possible.   Any undissolved portion, always small and occasionally nil, is filtered off and the solution added to that in flask D.   The solution is then transferred to a beaker and twice evaporated to dryness with hydrochloric acid to eliminate nitrates which may interfere with the barium sulphate precipitation.   This evaporation to dryness was not carried out when the method was first applied, but, as will be shown later, the results so obtained are too high owing to interference of nitrates.   The barium sulphate is determined in the ordinary way.   A hot solution of 3% barium chloride is added drop by drop to the hot sulphate solution acidified with hydrochloric acid.   With a sample of 0.2 to 0.3 gm. of wool excellent results were obtained by precipitating from a volume of about 40 cc. A few drops of acetone was added to the sulphate solution just before the addition of the barium chloride to facilitate the formation of a crystalline precipitate.   The precipitate was allowed to stand for one hour before filtering.

Blank determinations were carried out at regular intervals. The value of the blank depended entirely on the hydrogen peroxide used, and was constant for any one lot.

In certain cases the ash remaining in the tube P was analyzed separately for sulphur.

Experimental

Cleaning of Sample

Experiments showed that the most effective of the methods tried for cleaning the sample was to extract it in a Soxhlet apparatus and then wash it with distilled water.

Table I shows the sulphur content of samples cleaned by various procedures. The effect of thiophene and carbon disulphide in the benzene was investigated in order to determine whether sulphur-containing impurities in the solvent might be retained by the wool and result in erroneous values for the sulphur content.

It is evident that cleaning of the wool is best carried out by first extracting the wax with a solvent, and that the particular solvent or its purity is not of great importance.   For economy, petroleum ether was used as the solvent for

all other determinations. The final procedure adopted was to extract the
wool with petroleum ether in a Soxhlet for two hours or longer. This was
followed by washing with warm 0.1% saponin solution and then with distilled
water. After drying, the wool was teased out by hand and all extraneous
matter not removed in the washing, such as small bits of skin, leaves, straw

TABLE I

THE EFFECT OF VARYING THE WASHING PROCEDURE

Procedure	Per cent sulphur	Mean, %
*Low ⅓ Leicester (Alberta)**		
Washed in purified ethyl ether, 0.1% saponin solution and water, *A*	3.60 3.60 3.66 3.63	3.62
A re-extracted with ethyl ether	3.66 3.66	3.66
A re-extracted with ethyl ether and washed with water	3.64 3.68	3.66
A re-extracted with benzene (Merck's pure)	3.68 3.66	3.67
A re-extracted with benzene and washed with water	3.62 3.66 3.69	3.66
Washed with 0.1% saponin solution and water, *B*	3.58 3.55 3.60 3.54 3.59	3.57
Extracted with benzene (thiophene free),	3.67 3.64 3.64 3.59	3.64
Mixture of *A* and *C* re-extracted with benzene $+ 0.05\%$ thiophene, *D*	3.63 3.64 3.63	3.63
D after washing in 0.1% saponin solution and water	3.64 3.60 3.62	3.62
Mixture of *A* and *C* re-extracted with benzene $+ 0.05\%$ carbon disulphide	3.63 3.64 3.62 3.62	3.63

*Percentage of sulphur in the ash varied between 0.5 and 1.3% of the total sulphur; the mean for all determinations was 0.8%.

TABLE I—*Concluded*

THE EFFECT OF VARYING THE WASHING PROCEDURE—*Concluded*

Procedure	Per cent sulphur	Mean, %
Alberta fine Merino wool (1934 spring 64-66's)†		
Washed in bulk in benzene, 0.1% saponin solution and water, *A*	3.53	
	3.85	
	3.58	
	3.75	
	3.66	
	3.65	3.67
A extracted with pure ethyl ether	3.88	
	3.87	3.88
A extracted with benzene	3.84	
	3.90	
	3.92	
	3.89	3.89
Washed in purified ethyl ether, 0.1% saponin solution and water, *B*	3.88	
	3.88	
	3.81	
	3.92	
	3.87	3.87
Washed in unpurified ethyl ether, 0.1% saponin solution and water, *C*	3.87	
	3.88	
	3.92	
	3.86	
	3.89	3.88
A re-extracted with petroleum ether and washed in running water	3.90	
	3.87	3.89
Hampshire, ⅜ staple wool		
Extracted with petroleum ether, washed in 0.1% saponin solution and with water	3.31	
	3.31	
	3.29	3.30
Re-extracted with benzene and washed with water	3.33	
	3.30	
	3.31	3.31

†*Mean value for ash sulphur was 1.1% of total sulphur.*

In obtaining the above results, evaporation to dryness, to remove nitrates, was not carried out. All results are given on a dry-weight basis.

and tangled wool, was picked out. The wool was then re-extracted with petroleum ether, with alcohol and finally washed for five to six hours in warm running distilled water. Although tests showed that the extraction with alcohol did not appreciably affect the results, it was preferred to carry it out as a safety measure.

One of the wools was also soaked in dilute hydrochloric acid $(0.01\ N)$ for 24 hr., a procedure claimed by Marston (4) to be necessary. In confirmation of the results of Barritt and King (3), this procedure made no appreciable difference in the sulphur content found, as shown in Table II.

TABLE II

THE EFFECT OF PRETREATING WITH HYDROCHLORIC ACID

Procedure	Sulphur, %
No soaking in hydrochloric acid	4.12
Soaking in 0.01N hydrochloric acid, 24 hr.	4.08

Welsh wool (ref. X31) prepared according to standard procedure.

According to Marston, equilibrating with dilute hydrochloric acid removed inorganic sulphur, which is present as sulphate in appreciable quantities in many cases. In the combustion method this sulphur would remain in the tube as an ash. It will be noted that wherever the sulphur in the ash was determined separately, it was only about 1% of the total sulphur, so that large variations found in the sulphur content of various wools cannot be attributed to this factor.

Drying of Sample

Following the cleaning operations, the wool sample was dried to constant weight in a drying oven at 105° C. (two hours is generally sufficient), the wool being weighed without removal from the oven. This differs from the procedure followed by some other workers, whereby the wool is conditioned and the moisture content determined on a representative sample, the other samples employed for the sulphur determination being weighed in the conditioned state. However, tests carried out by the two methods showed that the dry weight obtained in the oven was slightly high (about 0.4%) compared with the dry weight calculated from the moisture content determined by the method of Barritt and King (2). This resulted in an apparent lowering of the sulphur content by 0.014% (actual content).

Tests also showed that heating at 105° C., for the time necessary to dry the sample, actually lowered the sulphur content by less than 0.04%. This lowering varies with different wools and may be nil in some cases. This seems to have been realized by other workers; for example, Barritt and King state (2) that they adopted the method of weighing the conditioned sample "to guard against the possibility that wool on drying out may lose volatile sulphur compounds, though this from experiments carried out appears to be improbable." It is likely that the particular wool that they investigated was of a type that gave the smaller difference.

The drying of the sample in the oven eliminates the necessity of conditioning it. This procedure is of advantage when the results are desired

in as short a time as possible and where conditioning facilities are not available. When utmost accuracy is required, it might be preferable to follow the method in which a regain determination is made on a separate sample. However, the error introduced by drying the sample in the oven is so small that the writers have considered this procedure satisfactory for general purposes, especially since the error can be largely reduced by applying a mean correction to the figures obtained. This mean correction, obtained from determinations on five different wools, is $+0.03\%$ actual sulphur.

TABLE III

THE EFFECT OF VARYING THE DRYING PROCEDURE

Procedure	Per cent sulphur					
	Leicester	South-down	N.Z. 40's	N.Z. 60's	Cheviot	Welsh $X31$
Standard, *(a)*	3.47_0	3.80_0	3.11_5	3.55_0	3.83_5	4.12_5
Conditioned sample, regain determined in large drying oven, *(b)*	3.48_5	—	3.12_0	3.58_5	3.87_5	4.13_5
Conditioned sample, regain determined by method of Barritt and King, *(c)*	3.50_0	3.81_5	3.13_5	3.59_5	3.89_0	4.15_0
Difference between *(c)* and *(b)*	0.01_5	—	0.01_5	0.01_0	0.01_5	0.01_5
Difference between *(c)* and *(a)*	0.03_0	0.01_5	0.02_0	0.04_5	0.05_5	0.02_5

The difference between *(c)* and *(b)* is due to the difference in the determined moisture content. It may be observed that the difference is fairly constant. The difference between *(b)* and *(a)* corresponds to the loss in sulphur during the drying, while the difference between *(c)* and *(a)* is the total error introduced by the drying method employed, and it has a mean value of 0.03_0.

Elimination of Nitrates

It has been stated earlier in the paper that it was found necessary to evaporate the hydrogen peroxide solution to dryness with hydrochloric acid in order to eliminate nitrates. This evaporation to dryness was carried out twice for each sample. Table IV gives the results obtained with various wools when this evaporation

TABLE IV

EFFECT OF EVAPORATION OF THE HYDROGEN PEROXIDE SOLUTION TO DRYNESS

Wool	No evaporation, per cent sulphur	With evaporation, per cent sulphur
Alberta Merino	3.88	3.75
Cheviot, $\frac{1}{4}$ staple	3.92	3.83
Romney, L-$\frac{1}{2}$	3.75	3.70
Hampshire, $\frac{3}{8}$	3.30	3.20
Kempy	3.59	3.45
Leicester, L-$\frac{1}{4}$	3.59	3.47

Mean difference, 0.11.

was not carried out, as compared with those obtained on double evaporation. It will be seen that, on the average, the results are 0.11% too high when the nitrates were not removed.

Comparison of Methods

Various wools were analyzed for sulphur by the Benedict-Denis (Barritt's modification (1)), the Carius, and the combustion methods for purpose of comparison. The Wool Industries Research Association analyzed and supplied five of these wools and also analysed two wools that the writers had sent them. Table V shows a summary of the results obtained.

TABLE V

COMPARISON OF METHODS

Sample	Combustion	Carius	Benedict-Denis	Wool Industries Research Association
Leicester L-$\frac{1}{2}$	3.47	3.46	—	
Southdown	3.79	—	3.79	
Western Australian Merino	3.57	3.58	3.53	3.73 (Benedict-Denis-Rimington)
Australian 70's	3.65	3.63	—	3.73 (Benedict-Denis-Barritt)
Welsh	4.02	3.92	3.97	3.92 (Carius)
Scotch Black Face	3.26	3.28	3.21	3.10 (Benedict-Denis-Rimington)
Welsh $X31$	4.12 (4.15)	4.08	4.00	4.15 (Benedict-Denis-Barritt)
				4.14 (Carius)
Suffolk	3.77 (3.80)	—	—	3.80 (Benedict-Denis-Barritt)
New Zealand 36's	3.16 (3.19)	—	—	3.20 (Benedict-Denis-Barritt)

NOTE:—*The figures in brackets are the corrected figures obtained when regain of separate samples is determined in a small drying oven.*

The agreement between the results obtained by the writers with the combustion and the Carius methods is, with one exception, very good. The Benedict-Denis method yielded results that were lower than those of the other two methods by about 0.05% (actual). The discrepancy between the values obtained for the Welsh wool by the Carius and those obtained by the combustion methods has not been explained. The determinations were repeated at various times and always with the same results. In view of the fairly constant difference between the values obtained by the Benedict-Denis and by the combustion methods, it would appear that the value for the Carius determination is, for some unknown reason, too low, although it is in agreement with that furnished by the W.I.R.A., which value was also obtained by the Carius method. Regarding the other values given by the W.I.R.A., it will be seen that there is good agreement for the last three wools. In these three cases the interval between the analyses carried out by the writers and those of the W.I.R.A. was comparatively short, but with the other wools the situation was different. The samples of Australian Merinos, for example, were more than one and one-half years old when analyzed by the writers, while the sample of Welsh wool was three years old or more.

The value given for the Scotch Black Face sample was determined by the Rimington modification of the Benedict-Denis method and this, according to Barritt (1), gives results 0.1 to 0.15% (actual) too low.

In order to point out the agreement obtained in several determinations on the same wool, typical sets of values for two different wools are given in Table VI.

The method was checked also by carrying out the determination with pure cystine. Found: 26.58, 26.50, 26.55, 26.60, 26.46, 26.58, 26.67%. Mean, 26.56%. Theoretical, 26.69%.

As 0.0001 gm. of barium sulphate in the determinations on cystine

TABLE VI

TYPICAL RESULTS

Wool	Per cent sulphur	Mean %
Leicester ¼ Blood	3.50	
	3.45	
	3.45	
	3.48	
	3.46	3.47
Cheviot	3.82	
	3.85	
	3.84	
	3.82	3.83

was equivalent to 0.05% actual sulphur content, the above figures are subject to an error of at least ±0.05%.

Advantages of the Method

Several methods have been proposed that would give satisfactory results for the determination of sulphur in wool. Of these the most widely used have been the Carius and the Benedict-Denis methods. A bomb method (1) has apparently also given good results. An electrolytic method has been used by Mossini (5).

A general review of the methods in use up to 1926 is given by Barritt and King (2). Up to that time they considered that the Carius method was the most satisfactory. However, the Carius method is generally recognized as being too laborious for ordinary purposes. The Benedict-Denis method is not easy to carry out, and the writers have found that great care is required to obtain concordant results. Complete and ready solubility of the ignited residue apparently depends on the conditions of ignition. The writers were unable to obtain complete solubility of this residue. This may account for the lower results that they obtained with this method. In the method are introduced metal salts, and these generally interfere in the sulphate precipitation. The bomb method, which makes use of sodium peroxide, is also open to this objection. Moreover, it is not easy to mix the wool thoroughly with the peroxide. A special apparatus is required and the removal of iron from the solution which is generally necessary is an added complexity. In the combustion method no foreign substance is present. There is no mixing to be done. The method is rapid and requires very little care apart from that generally necessary in analysis. Marston (4) has stated that sulphur estimation in organic materials is not easy, and that complete oxidation is well nigh impossible without a wet ashing process. The good results obtained by the combustion method do not bear out this contention.

If one may judge from the results given by Barritt (1) the deviation of the individual results is larger for the bomb method than for the Benedict-Denis method carried out with the nitric acid, but the writers have found the results of the combustion method to give a deviation even less than that given by the Benedict-Denis method.

Acknowledgment

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THE HEAT OF ADSORPTION OF OXYGEN ON CHARCOAL AT LOW SURFACE CONCENTRATIONS[1]

By MELVILLE J. MARSHALL[2] AND ALEXANDER S. MACINNES[3]

Abstract

The differential heat of adsorption of oxygen on activated cocoanut charcoal has been measured over the low concentration range to 14 micromoles per gram, by means of an improved ice calorimeter and a new charcoal bulb, in which oxygen is introduced into the middle of the charcoal mass. At zero concentration, a heat of adsorption of 129.0 kcal. per mole of oxygen was found, dropping to 72.0 kcal. at approximately 6.0 micromoles per gram. The initial heat of adsorption is much higher than the highest value that has been obtained previously. This indicates that the plain charcoal bulb previously used permitted loss of heat from the calorimeter; consequently, the values for the initial heats of adsorption were low. The theoretical significance of the high initial heat is discussed briefly.

Introduction

The differential heat of adsorption, at zero concentration, of oxygen on activated wood charcoal was found by Keyes and Marshall (5), using an ice calorimeter, to be 72.0 kcal. per mole. Later, Marshall and Bramston-Cook (7), using a larger quantity of activated cocoanut charcoal and an improved ice calorimeter, obtained the value 89.6 kcal. With the exception of these initial heats, the values obtained in the two investigations agreed reasonably well. This unusually high initial heat value made it of some interest to investigate in more detail the heats of adsorption over the low concentration range.

In 1934, Harold H. Herd (4), working in this laboratory, obtained with an improved apparatus an initial heat of adsorption of 95.3 kcal. In 1935, Harry Lotzkar (6), continuing the work of Herd, made four series of determinations. He obtained, for the initial heats, values varying from 75.3 to 89.3 kcal. These varying results led to the conclusion that either the more active part of the charcoal surface varied considerably after each outgassing, or some uncontrolled error still existed in the method of measuring the heat evolved. This variation could not be attributed to the existence of a slow chemical reaction following the apparently complete heat evolution, as the heat loss could be reproduced after about one hour for initial gas adsorptions. At higher concentrations the time of heat evolution is greater and the error should consequently be larger. In spite of this, the variation of heat of adsorption was most marked for the heat evolution resulting from the first addition of oxygen. Consequently, it was thought possible that this oxygen might be adsorbed entirely in the upper layers of the charcoal, and that this resulted in a relatively high temperature increase at a point in the charcoal where heat losses by radiation and convection would be most likely to occur.

To avoid this possibility in the present investigation, the silica bulb was altered in such a way that the oxygen could be introduced into the middle of the carbon mass instead of at the top as formerly (7). Smaller increments of oxygen were added, and the investigation was confined to a concentration range extending to 14 micromoles per gram.

Experimental

In the previous investigation (7) the charcoal was contained in a plain silica bulb joined to the remainder of the apparatus by means of a silica tube about 1.3 cm. in diameter. The charcoal was outgassed and the oxygen admitted through this one tube. The new bulb is shown in Fig. 1. The small silica tube, *B*, was fused into the charcoal bulb in such a way that it would not, by increasing the effective diameter, interfere with the insertion of the bulb into the calorimeter. The gas escaped from *B* into the charcoal through three small holes, each about 1 mm. in diameter. One hole was situated at the lower end of the tube *B*, and the other two were situated on opposite sides of the tube, as shown at *D*. In this way it was hoped to cause the oxygen to enter the charcoal at three points, and so obtain better distribution. The charcoal level is indicated by the dotted line at *C*. The highest hole was kept well below this level to ensure that none of the initial heat was generated on the upper surface of the charcoal. Tube *A* was connected, as before, by a short wide tube to the diffusion pump, in order to minimize resistance to the flow of gas at low pressures while the charcoal was outgassed. Tube *B* was connected directly to the gas pipette, for introduction of the oxygen. Graded silica-to-Pyrex seals were used for connecting both tubes to the remainder of the apparatus. The platinum lining of the original bulb was removed, as its advantages were doubtful, and the experimental difficulty of retaining it was considerable.
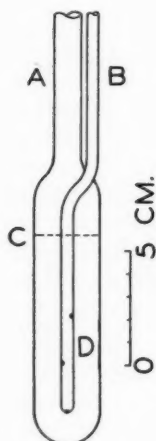
FIG. 1.
The charcoal bulb.

In the previous experiments (7), the space *C* in the calorimeter was filled with ice, and the voids between the pieces of ice were filled with distilled water. The use of water has since been found to be a disadvantage, as the ice floated to the top as it melted. This left the bottom of the calorimeter unprotected. In this investigation no water was used, but the ice was disturbed from time to time with a probe, and more ice was added when needed. One drawback to this arrangement was that the ice would melt away from the vertical part of the mercury capillary, and heat would flow down the mercury into the calorimeter. This was prevented by bending the capillary in a single horizontal loop, so that it encircled the neck of the calorimeter just above the rubber stopper, and thus ensured that the ice remain, owing to gravity, in contact with the lower part of the capillary.

A tendency of the mercury to stick to the walls of the capillary tube A (7) is responsible for some of the variation in the heat loss. In order to avoid this as much as possible, the capillary tube was wetted with water before the mercury was introduced. This decreased the heat value of the capillary per centimetre by 0.53% and caused the heat loss readings to be more nearly uniform, though some sticking of the mercury was still noticeable.

Mercury cutoffs replaced the stopcocks used previously (7). The two-way stopcock on the gas pipette J was of necessity retained, but it was protected by a mercury cutoff. As all adsorptions were made at very low pressures, the manometer H was removed and the small McLeod gauge replaced by one with a volume ratio of 10^{-5}.

The charcoal weighed 25.634 gm. and was identical with that used in the earlier investigation (7). With the exception of the changes mentioned previously, the method of operation of the calorimeter and the treatment of the charcoal were unaltered. In the present investigation the ice mantle was used for three weeks at a time, and was discarded only because of the necessity of outgassing the charcoal for a new series of determinations.

Results

The treatment of the results was similar to that previously followed (5, 7). The summation of the increments of heat, q, evolved in calories per gram of charcoal was plotted against the summation of the increments, c, of gas adsorbed in moles per gram of charcoal. The slope of the curve dq/dc at a point gives the differential heat of adsorption, Q, in calories per mole of oxygen at that point.

The experimental values of c and q are given in Table I. In Series 2 very small amounts of gas were employed, in order to approach zero concentration as closely as possible. The first value in this series falls on the q–c curve of

TABLE I
EXPERIMENTAL HEAT VALUES

Series 1				Series 2	
$c \times 10^6$	q	$c \times 10^6$	q	$c \times 10^6$	q
1.29	0.125	7.84	0.598	0.583	0.0673
2.70	0.229	9.91	0.746	1.149	0.1202
4.29	0.345	11.92	0.893	1.915	0.1825
6.05	0.467	13.82	1.031		

Series 1, while the second and third values lie slightly higher than the curve. However, the two series give the same initial heat value, and continue to agree exactly to about 0.6 micromoles per gram. It is by no means certain that complete agreement for the intermediate values is to be expected, as a small variation in the number of the most active spaces might easily occur at successive outgassings. If it is assumed that the heat evolution from each

of the most active spaces does not vary under these conditions, then variation in the number of spaces would not affect the initial heat of adsorption, but would affect the shape of the curve between the initial heat and the constant heat of 72.0 kcal.

The values of Q and c obtained from the q–c curve are given in Table II, and plotted in Fig. 2. Points are also shown for the values obtained by Herd (4), and for the values obtained by Marshall and Bramston-Cook (7), although no curves are drawn.

TABLE II

VARIATION OF DIFFERENTIAL HEATS OF ADSORPTION WITH CONCENTRATION

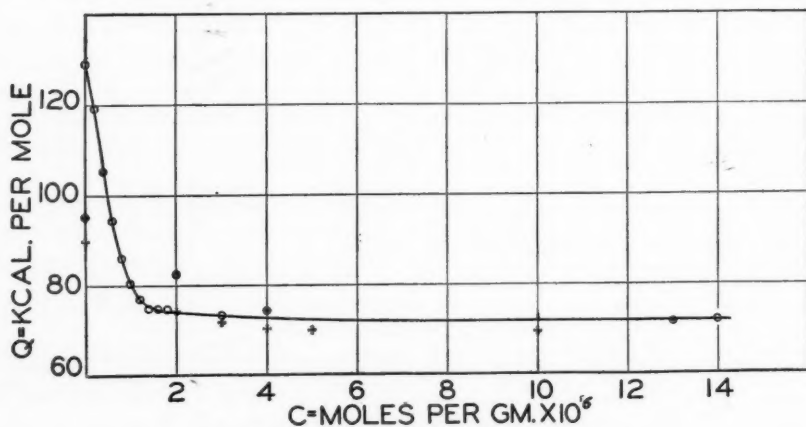| $c \times 10^6$	Q, kcal.	$c \times 10^6$	Q, kcal.	$c \times 10^6$	Q, kcal.
0.0	129.0	1.0	80.3	2.0	74.2
0.2	119.0	1.2	77.4	3.0	73.5
0.4	105.1	1.4	74.8	6.0	72.0
0.6	94.4	1.6	74.8	14.0	72.0
0.8	86.4	1.8	74.8		

FIG. 2.   ○, *MacInnes;* ●, *Herd;* +, *Bramston-Cook.*

Discussion

It will be noticed that the present results show a marked increase only for the initial heats of adsorption. For the higher concentrations they agree very well with the values obtained by Herd (4), while those obtained by Marshall and Bramston-Cook (7) are only slightly lower. The fact that only the initial heat is affected by the alteration in the silica bulb seems to verify reasonably well the previous assumption that a certain fraction of the initial heat had escaped from the calorimeter in the earlier investigations. This confirms the observation of Bull, Hall and Garner (2) that the initial

quantity of oxygen added is adsorbed almost completely in the part of the charcoal with which it first comes in contact. They found that this led to considerable error for the initial heat when a thermocouple calorimeter was used. Until the above-mentioned difficulties with the initial heat were encountered, the present writers were of the opinion that this effect would produce no error whatever with the ice calorimeter, as the ice mantle extended a considerable distance above the level of the charcoal, and it was considered adequate to absorb all the heat, no matter where the heat was liberated.

The constant heat of adsorption of 72.0 kcal. agrees with the original value obtained by Keyes and Marshall (5) as well as with that obtained by Herd (4) in this laboratory. This value is probably more accurate than the value of 70.0 kcal. obtained by Marshall and Bramston-Cook (7). Since Bull, Hall and Garner (2). also obtain a flattening of the curve in the vicinity of this point, the reality of this constant heat can now be considered to be definitely established. The significance of this constant value is still a matter for speculation.

While the initial heat of adsorption is much higher than that previously obtained, it is still below the high heats of about 200.0 kcal. obtained by Garner and his co-workers (1, 3, 8) at higher temperatures, or the still higher heats which can be calculated on the assumption that the surface bonds are equal in strength to those of an atom of gaseous carbon (3, 5). An exact estimate of a theoretical value for the initial heat of adsorption is not possible at the present time, as neither carbon monoxide nor carbon dioxide is formed at $0°$ C., and the heats of formation of surface compounds, consisting of oxygen atoms combined chemically with the carbon atoms at the surface in various definite ways, are unknown. In view of these considerations, there is no reason why the initial heat of adsorption should not be greater than 96.4 kcal., the heat of formation of carbon dioxide from charcoal.

The possibilities exist for the formation, on the surface, of complexes corresponding to compounds containing carbon and oxygen in ratios quite unknown in the normal state. Such a complex high in carbon could give rise to the high initial heat of adsorption, while a decrease in the carbon to oxygen ratio, owing to an increase in the oxygen concentration, could give the lower heats of about 72.0 kcal. However, further speculation will be deferred until new pressure equilibrium data, now being accumulated in this laboratory, are available. It is hoped to use the present results, in conjunction with these data, to throw more light on this rather complicated problem.

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THE EFFECT OF PRETREATING WOOD IN AQUEOUS SALT SOLUTIONS ON SUBSEQUENT DELIGNIFICATION IN SULPHITE LIQUOR[1]

By J. M. CALHOUN[2] AND O. MAASS[3]

Abstract

The pretreatment of spruce wood in various neutral salt solutions was found to retard subsequent delignification in sulphite liquor to an extent depending upon the position of the ions of the salt in the lyotropic series. Increase in the salt concentration increased the effect of pretreatment.

Introduction

Corey and Maass (1) have described the effect of pretreating spruce wood in buffer solutions of various hydrogen ion concentrations on subsequent sulphite cooking. They found that delignification was retarded to an amount depending on the pH of the pretreating solution; the effect was a minimum at pH 5 and increased at lower and higher hydrogen ion concentrations. The explanation offered to account for the phenomena was that an agglomeration of the lignin particles took place, and that this rendered subsequent cooking more difficult.

It has since been found that pretreatment with different buffers at the same pH gives different results. This led to an investigation of the effect of pretreatment with various neutral salt solutions. Although the hydrogen ion concentration of different buffers may change at cooking temperatures in a different manner, evidence is presented which indicates that other factors must be considered before any satisfactory explanation of the pretreatment phenomena can be made.

Experimental

Portions of spruce wood-meal, 40-100 mesh, density 0.34, lignin 29.0%,[*] with solutions of various salts, were sealed in bronze bombs and heated, at the cooking temperature, in a well stirred glycoline bath for a definite time. The pH of the pretreating solution was checked at room temperature by means of a quinhydrone electrode, before and after heating. The meal was washed free of salt solution, air dried and then cooked in calcium bisulphite liquor containing 5.1% of total, and 1.2% of combined, sulphur dioxide. The resulting pulps were analyzed for both lignin and sulphur.

Discussion

Tables I and II show the effect of pretreating spruce wood with various potassium salts and chlorides arranged in order of the residual lignin content of the pulps. A run without pretreatment and one with pretreatment with

TABLE I
EFFECT OF ANIONS IN PRETREATMENT
Pretreatment: **6 hr., 140° C.**; cooking 3 hr., 140° C.

| Pretreating solution 1.0 molar	Yield of pulp, %	Yield of carbohydrate, %	Lignin as % of original wood	Sulphur as % of lignin
No pretreatment	47.4	45.9	1.48	13.4
Pretreated with water only	59.2	47.4	11.8	—
KCNS	68.6	46.6	22.0	4.58
KI	60.2	46.2	14.0	5.32
KBr	60.2	48.0	12.2	—
KNO$_3$	59.7	47.6	12.1	5.54
KCl	58.6	47.3	11.2	5.98
KH$_2$PO$_4$	59.7	49.7	9.95	6.18
K$_2$SO$_4$	57.1	48.0	9.10	5.91

TABLE II
EFFECT OF CATIONS IN PRETREATMENT
Pretreatment: 6 hr., 140° C.; cooking 3 hr., 140° C.

Pretreating solution 1.0 molar	Yield of pulp, %	Yield of carbohydrate, %	Lignin as % of original wood	Sulphur as % of lignin
NH$_4$NO$_3$	67.2	43.6	23.6	3.47
NH$_4$Cl	66.9	44.1	22.8	3.79
SrCl$_2$	64.4	46.3	18.1	4.23
CaCl$_2$	63.0	45.7	17.8	—
BaCl$_2$	63.5	46.6	16.9	4.83
MgCl$_2$	61.5	47.3	14.2	5.23
LiCl	61.3	48.2	13.1	5.63
NaCl	59.0	47.3	11.7	5.77
KCl	58.6	47.3	11.2	5.98

water only serves as a comparison. The pH of the pretreating solutions in each case was found to be well within the range pH 4 to pH 6 which Corey and Maass (1) have shown to have a minimum effect on pretreatment. Hence, the results obtained cannot be attributed to differences in hydrogen ion concentration of the different salt solutions.

It may be noticed that in almost every case the sulphur content of the lignin varies inversely as the lignin content of the pulps. This indicates that pretreatment hinders sulphonation of the lignin rather than the hydrolysis of sulphonated lignin, although probably both reactions are affected.

The close connection between the observed order of the anions and cations in pretreatment and the lyotropic series is apparent at once. The order of the lyotropic series given by Traube (5) is:

(a) For the hydration of ions:

CNS < I   < Br   < NO$_3$ < Cl   < HPO$_4$ < SO$_4$

Ba < Sr < Ca < Mg ; NH$_4$ < K   < Na < Li
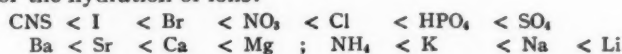
(b) For the swelling of gelatin:

CNS > I   > Br > NO$_3$ > Cl   > SO$_4$

The observed order of the anions in pretreatment is the reverse of that for the hydration of the ions, but the same as that for the swelling of gelatin. This suggests that swelling may play a part in the phenomena.

The order found for the cations in pretreatment does not agree as well with the lyotropic series. The observed order for the alkaline earth metals is the reverse of that for hydrate formation, while the observed order for the alkali metals is the same as the order for hydrate formation. The effect of NH_4^+ is entirely out of proportion to its position in the lyotropic series, although ammonium nitrate has a greater effect than ammonium chloride. This shows the lyotropic effect of the anion. It is believed that ammonium compounds may have a specific action on lignin.

Table III and Fig. 1 show the effect of varying the concentration of potassium thiocyanate in the pretreating solution. The retarding of subsequent delignification increases rapidly with the concentration of the salt, and again it can be seen that the sulphur content of the lignin is inversely proportional to the residual lignin content of the pulp.
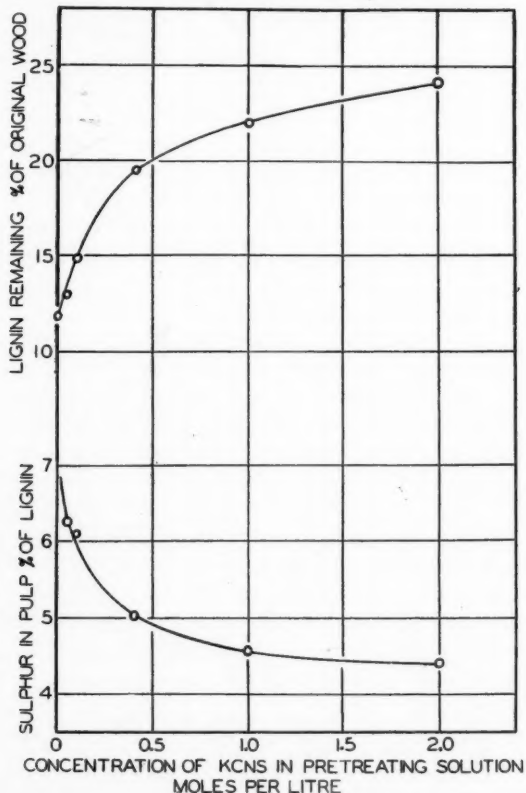

FIG. 1. *Effect of concentration of potassium thiocyanate in pretreating solution on subsequent delignification.*

TABLE III

EFFECT OF CONCENTRATION OF POTASSIUM
THIOCYANATE IN PRETREATMENT

Pretreatment: 6 hr., 140° C.; cooking 3 hr., 140° C.

Concentration of KCNS, moles per litre	Yield of pulp, %	Yield of carbohydrate, %	Lignin as % of original wood	Sulphur as % of lignin
0.0	59.2	47.4	11.8	—
0.05	61.5	48.6	12.9	6.26
0.10	63.4	48.6	14.8	6.12
0.40	66.0	46.5	19.5	5.02
1.0	68.6	46.6	22.0	4.58
2.0	70.4	46.2	24.2	4.42

The influence of the lyotropic series on numerous physical chemical properties of solutions and lyophilic colloids has long been known. The explanation of the phenomena in the present case is not so clear. Stamm (4) has shown that the saturated solutions of chloride and potassium salts cause a swelling of wood and other cellulosic materials at room temperature, beyond the normal water-swollen state, in the following order:

$$Zn > Li > Ca > Mg > Mn > Ba > Na > NH_4 > K$$
$$CNS > I > CrO_4 > Br > Cl > NO_3 > SO_4 > CO_3$$
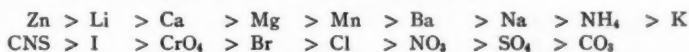
Decrease in the salt concentration decreases the extent of swelling. According to Herzog and Beck (2), saturated solutions cause a peptization or partial solution of cellulose at temperatures above 135° C., in the order:

$$Ca > Ba ; Li > Na > K > NH_4$$
$$CNS > I > Br > NO_3 > SO_4$$
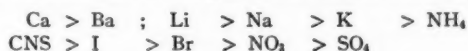
At the present stage of the investigation, it cannot be stated whether swelling or peptization or both play a part in the pretreatment phenomena. It can be pointed out only that the influence of the lyotropic series is similar in all three cases. Any satisfactory explanation must also account for the effect of varying the hydrogen ion concentration of the pretreating solution, as observed by Corey and Maass. It has been shown by Stamm (4) that the swelling of wood is independent of pH except in very alkaline solutions. However, it has been shown here that the problem is intimately connected with the colloidal nature of lignin and cellulose, and it is hoped that work under way will throw more light on the subject of pretreatment and thus indirectly on the mechanism of sulphite pulping.

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THE NATURAL OCCURRENCE OF ACETYL-ORNITHINE[1]

By Richard H. F. Manske[2]

Abstract

The tap-roots of *Corydalis ochotensis* were found to contain a relatively large amount (10%) of an amino-acid, the chemical examination of which disclosed it to be the hitherto unknown *mono-acetyl-d-ornithine*. Although acyl and aroyl derivatives of amino-acids have long been recognized as animal catabolites, such derivatives do not appear to have been previously observed as plant anabolites.

The author has been engaged upon a program of research, the primary object of which is the elucidation of the nature of the alkaloids of a number of plants belonging to the Natural Family Fumariaceae. Some twenty species have been investigated in whole or in part. In many cases, thus far unreported by-products such as sterols, sterolins, alcohols and other neutral substances, have been isolated. It is proposed to place on record a miscellany of these observations on some future occasion. The present case seemed of sufficient interest to warrant a separate record.

Corydalis ochotensis Turcz. is a native of the vicinity bordering the Sea of Okotsk in Eastern Siberia. It appears to be an obligate biennial, producing during the first year of its growth a fleshy sub-tuberous tap-root, 12 to 16 cm. in length, which during the second year of growth to maturity sends out numerous fibrous roots. In this process the original tap-root itself shrinks to a somewhat insignificant primary root. The main stem as well as the branches and petioles are irregularly tetragonal in cross section. The ultimate segments of the compound leaves are almost circular in outline. The seed pod is flat and curved. At maturity it is under stress and discharges the black seeds with considerable force when disturbed. The entire plant is glaucous green and the much branched and reclining stem may attain a length of 1 to 1.5 metres (5).

The material for the present work was grown in a local garden from seed obtained through the courtesy of Mr. John Adams, Botanist at the Central Experimental Farm, Ottawa. After the first year of growth the plants were collected and the leaves severed from the roots. The latter after washing and drying were ground to a coarse powder. Following the usual procedure, the material was extracted in a Soxhlet apparatus with methanol. During the course of this extraction a substance crystallized from the hot extract in large stout crystals which had the appearance and taste of sucrose. After cooling, filtering and washing thoroughly with methanol the yield of product based on the weight of air-dried roots was 10%.

It soon became evident that this substance was not sucrose, and in fact it was found to contain nitrogen. This observation together with its strong sweet taste suggested an amino-acid, and the test with triketo-hydrindene hydrate (ninhydrin) gave an intense blue color even in very dilute solution. Kjeldahl analysis showed 15.4% nitrogen and a van Slyke amino-nitrogen determination gave 9.2%. The well crystallized copper salt contained 14.9% copper and 13.1% nitrogen. These figures indicate a copper to nitrogen ratio of 1 to 4 and an amino-nitrogen to total nitrogen ratio of 1 to 2. Further, on the basis of a mono-basic acid, the molecular weight is 172 or 174 corresponding to $C_7H_{12}O_3N_2$ or $C_7H_{14}O_3N_2$ respectively. Such a substance could be a dipeptide but none appeared to have been described which might be regarded as identical with it.

An attempt was therefore made to hydrolyze it with dilute sulphuric acid in order to identify the hydrolytic fragments. Unexpectedly, however, acetic acid proved to be one of the hydrolytic products. On the basis therefore of the $C_7H_{14}O_3N_2$ formula the second fragment must be $C_5H_{12}O_2N_2$, that is, ornithine or an isomeric diamino-valeric acid. Removal of the sulphuric acid from the hydrolyzed solution by means of baryta yielded a strongly basic solution of the amino-acid. This readily dissolved in methanol and yielded a picrate melting at 207° C.* Riesser (6) gives 198–199° (?corr.) for the melting point of d-ornithine picrate. An authentic specimen of d-ornithine picrate which melted at 207° C. was kindly supplied by Dr. H. B. Vickery, Connecticut Agricultural Experiment Station, New Haven, Conn., and in admixture there was no depression in the melting point. The substance therefore is mono-acetyl-d-ornithine, $CH_3 . CO . NH . CH_2 . CH_2 . CH_2 . CH(NH_2) . CO_2H$. The alternative position for the acetyl group is excluded because of the positive ninhydrin reaction and presumably also because of the sweet taste of the substance. The positive rotation of 13.1° clearly relates this amino-acid to natural d-arginine and d-ornithine.

The author is not familiar with an analogous case in the domain of phytochemistry. There does not appear to be any good reason why ornithine should be the chief nitrogen requirement of this particular plant and, further, why an acyl derivative should be the choice. Acyl and aroyl derivatives of amino-acids are animal catabolites and serve to eliminate injurious acids from the animal body. Dibenzoyl-ornithine (ornithuric acid) and hippuric acid play this role in birds and mammals respectively for the elimination of benzoic acid. In the case of C. ochotensis, however, acetyl-ornithine can be regarded only as an intermediate metabolic product serving as a nitrogen reservoir.

It may be added that ornithine plays an important role in the well known mechanism which Robinson (7) has advanced to account for the phytosynthesis of alkaloids from amino-acids, and it may be significant that this particular plant does elaborate a number of alkaloids. Many workers have

* Melting points are corrected.

investigated the non-protein, non-alkaloidal nitrogenous substances in plants, but the author is not aware of such an investigation of a plant known to contain alkaloids except perhaps tobacco. Free amino-acids are of fairly common occurrence, but they appear to be used as a vehicle for translocating nitrogen and not as nitrogen reservoirs. The latter role is traditionally played by proteins, and the amides asparagine and glutamine.

Dr. Vickery, to whom this paper has been submitted, has kindly prepared some comments of which the following is a summary.

"The general behaviour of the plant makes it appear possible that acetyl-ornithine is the substance utilized to care for an accumulation of a highly basic constituent which, if present in the free form, might become toxic through its influence on the pH. This would be closely analogous to the manner in which the beet root cares for an excessive quantity of ammonia by converting it into glutamine.

"In pursuit of this speculation the metabolism of the plant may involve an accumulation of arginine and the co-presence of arginase, so that the tissue may contain not only ornithine but urea as well. It would seem logical therefore to look for evidence of the presence of arginase and of urease and urea.

"Should urease be present, then the root should store not only the ornithine but also either asparagine or glutamine since the ammonia would be detoxicated by the synthesis of one of these amides.

"From this point of view one would perhaps question the implication that acetyl-ornithine is the chief nitrogen requirement of this particular plant. . . . ."

The questions here raised can be decided only by further work, and it is hoped that when more material becomes available some of the moot points may be clarified.

Experimental

Mono-acetyl-ornithine

The crude acetyl-ornithine, obtained as described above, was dissolved in water and the turbid solution filtered with the aid of infusorial earth and charcoal. A small amount of colloidal matter made this filtration extremely difficult and tedious. Even the filtrate retained a turbidity which could not be completely removed by further filtration. The colorless solution was evaporated *in vacuo* to incipient crystallization and then treated with hot methanol. The finely crystalline material was filtered off and washed with cold methanol. Further purification, and the elimination of all but a trace of ash, was accomplished by recrystallizing from methanol in a Soxhlet apparatus, the chief objection here being the vigorous bumping which occurred when some of the substance had crystallized in the extract. As thus obtained, mono-acetyl-ornithine consisted of colorless fine plates which melt with decomposition at 266° C. $[\alpha]_D^{24} = +13.1°[c = 4$ in water]. Calcd. for $C_7H_{14}O_3N_2$; C, 48.28; H, 8.05; N, 16.1; amino-N, 8.1%. Found: C, 48.30; H, 7.85; N, 15.4; Amino-N, 9.2%.

Acetyl-ornithine gives a precipitate with phosphotungstic acid, but not with mercuric chloride, picric acid or flavianic acid.

The copper salt was prepared by boiling a suspension of copper carbonate in an aqueous solution of the acid. It crystallized from the concentrated solution while still hot and was recrystallized from a large volume of hot water. Pale blue plates were thus obtained. The substance is only slightly soluble in cold water. Calcd. for $C_{14}H_{26}O_6N_4Cu, H_2O$; Cu, 14.9; N, 13.1%. Found: Cu, 14.9; N, 13.1%.

Hydrolysis

Three grams of the amino-acid was dissolved in 25 cc. of water to which 5 gm. of concentrated sulphuric acid had been added. The solution was heated to boiling and then left on a steam bath overnight in a loosely stoppered flask. A pronounced odor of acetic acid had developed. The solution was evaporated to a small volume *in vacuo* and the acetic acid identified as follows: The distillate was neutralized with a measured amount of potassium hydroxide and evaporated to dryness on a steam bath. The saline residue was dissolved in a small volume of water and heated for an hour on the steam bath with an ethanolic solution of xenacyl bromide containing 75% of the calculated amount. On cooling, the xenacyl acetate crystallized in colorless flat plates melting at 111° C. Drake and Bronitsky record the same melting point (1).

The residue from which the acetic acid had been distilled was diluted with water and again evaporated *in vacuo*. The aqueous solution of the residual syrup was then quantitatively freed of sulphuric acid by means of barium hydroxide, and the colorless filtrate evaporated to dryness *in vacuo*. This was dissolved in methanol and a small amount of insoluble residue removed by filtration. A portion of the filtrate was treated with a methanolic solution of picric acid. On evaporation to a small volume, ornithine picrate crystallized in pale-orange fine prisms sparingly soluble in methanol. It melted at 207° C. after one recrystallization from hot water, and in admixture with an authentic specimen of *d*-ornithine picrate which melted at the same temperature there was no depression in melting point.

Dibenzoyl-ornithine

A mixture of ornithine and its carbonate obtained from the acetyl-compound was benzoylated with benzoyl chloride in alkaline solution by Fischer's method. The recrystallized dibenzoyl-ornithine melted at 189° C. Fischer (2) gives the melting point as 187–188° C. corr. (184° C. uncorr.). Jaffé (3, 4) gives 182° C., presumably uncorrected.

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